WITH THE NAME OF GOD
THE MOST GRACIOUS, THE MOST MERCIFUL

THERMAL DEGRADATION STUDIES OF ALTERNATING COPOLYMERS AND THEIR RELATED HOMOPOLYMERS

by:

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In memory of my Grand Mother

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CONTENTS

CHAPTER SEVEN. THERMAL DEGRADATION STUDY OF THE ALTERNATING COPOLYMER OF VINYL ACETATE AND CROTONIC ACID

CHAPTER EIGHT. THERMAL DEGRADATION STUDY OF POLY(ISOPROPENYL ACETATE)

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SUMMARY

Alternating copolymers posses a uniquely regular chain structure in which the two different type of monomer (A and B) units present in strictly alternating ordered sequence in the chain backbone, i.e. —ABABABABA— . These types of material have a novel macromolecular structure. Their thermal degradation behaviour remains largely unexplored and it was the interest in the present research to discover what are the patterns of behaviour and how they compare with those of random copolymers. For the aforesaid reasons, various alternating copolymers and their related homopolymers were synthesised, characterised and their thermal degradation behaviour was studied under programmed and isothermal heating experiments using TVA, TG and DSC techniques.

A general description of major types of degradation processes which may occur during thermal decomposition is described in Chapter 1. The brief description of thermal degradation behaviour of the alternating copolymers is also included in this Chapter.

Chapter 2 summarises the application and experimental techniques employed in the present study. The first part deals with the thermal analysis techniques and the second part describes the techniques used to identify the degradation products both quantitatively and qualitatively.

Monomer preparation, polymerisation and characterisation of monomers is considered in detail in Chapter 3. This also includes a brief description of the calculation determination of monomer feed for the preparation for the copolymers.

Vinyl acetate, isopropenyl acetate and methacrylic acid were used in several alternating systems, so it was appropriate to consider the thermal degradation behaviour of these monomers as homopolymer. The thermal

degradation behaviour of poly(vinyl acetate) PVA and poly(isopropenyl acetate), PIPAc are described in Chapter 4 and 8. The two homopolymers show degradation features in common. Both show a two stage decomposition under programmed heating, the first involves the elimination of acetic acid in a zipper deacetylation of short zip length. The second stage reaction, occurring at higher temperatures, involves fragmentation of the backbone and the formation of aromatics and cold ring fraction. Chain scission is much more extensive in the case of PIPAc than for PVA, because all the acetate groups are linked to the tertiary C atom, which is considered as a initiation point for the thermal degradation. Hence thermal dissociation is very easy in the case of PIPAc which makes polymer thermally less resistant.

In Chapter 5, the studies of the thermal decomposition of poly(methacrylic acid), PMAA are described. PMAA exhibits two decomposition stages. In the first stage, there is intra- and inter molecular anhydride formation between COOH groups with water elimination. In the second stage, between 350 and 500°C, the polyanhydride decomposes with scission through a random process leading to large fragments that constitutes the tar. In comparison with all three homopolymers, PMAA has good thermal stability, inspite of its methyl branches. The stability is due to the large scale of anhydrisation.

The thermal behaviour of vinyl acetate with methacrylic acid copolymer (VA-MAA) is examined in Chapter 6. The VA—MAA copolymer, containing about 65% of alternating units, suffers dehydration leading to anhydride, as in PMAA, but the anhydride formation competes with the formation of lactone rings between adjacent acid and ester units. The formation of the lactone rings puts strain on the macromolecular chain, triggering the early decomposition of the anhydride rings, which in turn leads to the decomposition of the whole system. Degradation with the massive weight loss is swift, the polymer being extensively (95%) decomposed by 425°C.

The lactone formed in the copolymer is a highly resistance species. It decomposed around at 480°C, helping the polycondensation of the aromatic rings.

In Chapter 7, the thermal stability and degradation behaviour of crotonic acid and vinyl acetate alternating copolymer is discussed. The CA—VA copolymer thermally decomposes in two well separated stages as the temperature is raised. In the first stage the main reaction is cyclisation of adjacent acetate and acid side groups with the elimination of acetic acid and the formation of γ-lactone rings. It has been evaluated that two thirds of the ester and acid groups participate in lactone formation. In a secondary reaction, decarboxylation of acid groups occur with the elimination of CO_2. In the second stage, the main reaction is lactone decomposition leading to extensive chain scission. There is only 3% ultimate residue at 500°C. Compared to poly(vinyl acetate), the CA—VA alternating copolymer has a lower resistance to thermal degradation.

The thermal degradation behaviour of the alternating copolymer of maleic anhydride with isopropenyl acetate (MAn—IPAc) is considered in Chapter 9. The MAn—IPAc copolymer breakdown occurs in two well defined stages. In the first stage, nearly all the acetate side groups are lost in the formation of acetic acid and the development of unsaturation. This is confirmed by examination of the IR spectra of the partially degraded copolymer. The second stage of degradation starts with the breakdown of the anhydride rings to CO_2 and CO, followed by the formation of tar, char and some volatile aromatics, as the backbone breaks up. The mass balance measurements indicate that the polymer degrades to a large liquid and cold ring fraction and to moderate gas and char fraction. The MAn—IPAc copolymer allows formation of a novel macromolecular structure by controlled degradation at a lower temperature.

In Chapter 10, the thermal stability and degradation behaviour of the alternating copolymer of allyl acetate and maleic anhydride are discussed. This material is isomeric in structure with MAn—IPAc copolymer but shows very different stability and decomposition behaviour. The TVA curve for the copolymer shows a series of overlapping decomposition reactions, starting from 200°C and that initially only CO_2 is evolved. The acetic acid which is the major product begins to be released some time after the decarboxylation reaction. This is the striking contrast to the behaviour in the MAn—VA and MAn—IPAc copolymers, where the acetic acid is the initial product. Significant minor products above 300°C include five membered ring ketones and γ-lactones, plus some aromatics.

The decomposition of the maleic anhydride and allyl acetate (MAn—AllAc) copolymer is very complex. The dominant processes can, however, be summarised in terms of low temperature reaction generating CO_2 and forming ketonic structures in the backbone, and a higher temperature reaction leading to acetic acid and CO and forming cyclic lactone in the chain. These are followed by break up of the modified polymer chain in the temperature region 350—500°C.

CHAPTER ONE

INTRODUCTION

HISTORY OF POLYMER SCIENCE

Polymers are large molecules made up of relatively simple repeating units. These can take the form of long linear chains, or large crosslinked networks. The true nature of these macromolecules however, only become understood in the 1920s largely because of the efforts of Staudinger (1) who proposed the idea that polymers are not just physical aggregates of small molecules but, in fact, they are composed of very large molecules containing long sequences of simple chemical units linked together by covalent bonds.

Materials of this type can be found in nature, e.g. rubber, cellulose, protein, resins and gums, but polymers can also be produced synthetically. The first synthetic polymer was 'Bakelite' made from phenol and formaldehyde by Baekland in 1909. Carothers (2, 3) in 1930 carried out important work preparing macromolecules from organic preparations and correlated the properties of the polymer with the molecular structure. Since then, new polymers have appeared with increasingly better properties from the world over.

As the properties of the synthetic polymers have improved, they have become increasingly important as construction materials, as they can be manipulated easily and the properties can be matched to the task in hand.

The properties can be controlled by using various monomers in the polymerisation step or by the use of additives, for example fillers, flame retardants, plasticisers, etc.

When a polymer is made from a single type of monomer this is said to be a homopolymer. However, it is also possible to polymerise two or more types of monomer together so that both are incorporated into the same chains. These are said to be copolymers. The proportions and type of reactants can be adjusted, resulting in the possibility of forming an infinite variety of polymers. Thus it should be possible to manufacture materials with properties specific for any purpose.

Copolymerisation is the most general and powerful method of effecting systematic changes in polymer properties, and is widely used in the production of commercial polymers. Copolymerisation modifies the symmetry of the polymer chain and modulates both intermolecular and intramolecular forces, so the properties such as melting point, glass temperature, crystallinity, solubility, elasticity, permeability and chemical reactivity may be varied within wide limits.

Copolymers can be classified into a number of groups, such as random, graft, ladder and alternating copolymers but the research reported concerns alternating copolymers so these will be discussed in detail.

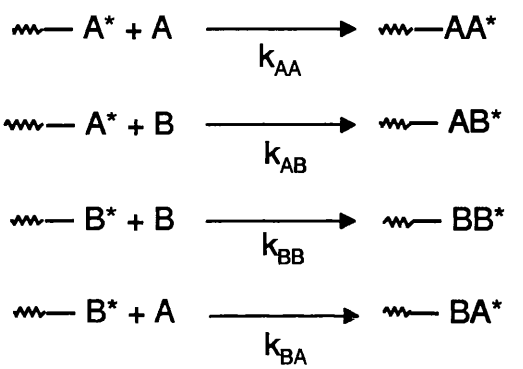
Alternating Copolymers

Alternating copolymers possess a uniquely regular chain structure in which the two different types of monomer units, denoted A and B alternate along the polymer chain, to give a copolymer with structure as shown below.

—ABABABABABABABABAB—

In alternating copolymerisation ideally no monomer will homopolymerise, i.e. there shall not be two similar monomer units adjacent.

This is dependent upon the reactivity ratios for any monomer pair which are the ratios of the rate constants of the different propagation reactions. In binary copolymerisation there are four possible propagation reactions, with associated rate constants (k).



The reactivity ratio for monomer A (r_A) is k_{AA}/k_{AB} and the reactivity ratio for monomer B (r_B) is k_{BB}/k_{BA}. The value of r is therefore a measure of the preference for an active centre to add on a monomer of its own type rather than to add on a monomer of the opposite type. The values of r_A and r_B, together with the monomer feed composition, determine the composition of the copolymer.

To obtain a perfect by alternating copolymer the reactivity ratios (r_A and r_B) should be zero, but very few monomer pairs exhibit this behaviour exactly. Many other monomer pairs can give an essentially alternating copolymer if at least one of the monomers has an extremely low reactivity ratio. For example, maleic anhydride and fumaric acid and their esters and anhydrides do not homopolymerise, but tend to give alternating copolymers with a wide variety of comonomers.

THERMAL DEGRADATION OF POLYMERS

Degradation of polymers is defined conventionally as deterioration through the chemical reaction of those physical properties which make them commercially useful. But in a general sense it may be made to cover all reactions of polymers. During the last few decades the effect of the heat at elevated temperatures on the stability of natural and synthetic polymers has aroused interest and has been investigated more extensively than that of any other energy-transfer agent, such as light, mechanical impact, ultrasonic waves, or infrared, ultraviolet, or gamma radiation (4,5).

From the scientific point of view, a knowledge of thermal behaviour of polymers can help to reveal the structure, such as the sequence and arrangement of the repeating units and side groups in the polymer chain, and possibly also the nature of the chain ends and the presence of crosslinks.

More importantly, thermal degradation studies of polymers are of extreme importance from a practical point of view, as they not only explain the behaviour of polymers under conditions of high temperature but also help in selecting the right kind of material for specific uses where high temperatures are encountered.

Polymers can suffer degradation during fabrication processes that involve heating, such as extrusion or moulding. The polymer may not be able to withstand the temperature required and it may degrade. In this case it is most desirable to know the threshold temperature of polymer breakdown which is the upper limit of temperature of fabrication.

It is also important to know about any toxic volatile products of degradation in order to guarantee the safety of workers (6).

The detailed analysis of degradation products is also essential in relation to flammability and the possible evolution of toxic products during incineration of plastic waste.

Thermal degradation studies are also helpful in suggesting the design and syntheses of new materials to meet new or existing requirements.

In this present work the thermal stability and degradation of various polymer systems will be examined, so it is essential to know the main types of reactions which can occur during the degradation process.

CLASSIFICATION OF REACTION TYPES

The thermal degradation mechanisms of polymers can be can be classified (7) into two main groups: chain scission (depolymerisation) and non-chain scission (side group reactions).

The reaction mechanism can be radical or non-radical and the path followed depends on the chemical nature of the species involved.

Chain Scission or Depolymerisation

Chain scission reactions are characterised by breaking of the polymer chain backbone, producing smaller chain fragments. Ultimately, the products will be monomer or substances closely related to it, and the residue will retain the chemical characteristics of the parent material.

A large variety of addition polymers depolymerise thermally, which can occur in one of two possible ways.

Firstly, degradation initiated by homolytic scission may then proceed by an unzipping process to produce large amounts of monomer. Poly(methyl methacrylate) and poly(alpha methylstyrene) are among the few examples of polymers that will degrade almost completely to monomer.

Alternatively, random chain scission, i.e. scission at any place throughout the chain either by a radical route or non radical route can occur. For example, polypropylene (PP) and polyethylene (PE) give negligible yields of monomer (8-10), as a result of the predominance of random scission.

However some polymers show both reaction types. Polystyrene does this with both intramolecular transfer giving styrene oligomers and depolymerisation giving 40 to 50% of monomers depending on experimental conditions (11, 12). The occurrence of transfer, either inter- or intra molecular leads to non-monomeric material and thus reduces the monomer yield.

Radical Depolymerisation

The thermal degradation of poly(methyl methacrylate) PMMA, was studied extensively by Grassie and his associates (13, 14, 15). The effect of pyrolysis on the molecular weight of PMMA samples at different temperatures was examined and a quantitative yield of monomer was obtained. They discovered that the thermal degradation of PMMA at low temperature involves the production of free radicals from unsaturated chain ends, while at high temperatures free radicals are produced through random chain scission, followed in each case by unzipping to monomer. Termination of the unzipping reaction can only occur by interaction of pairs of radicals or when the ends of the chain is reached.

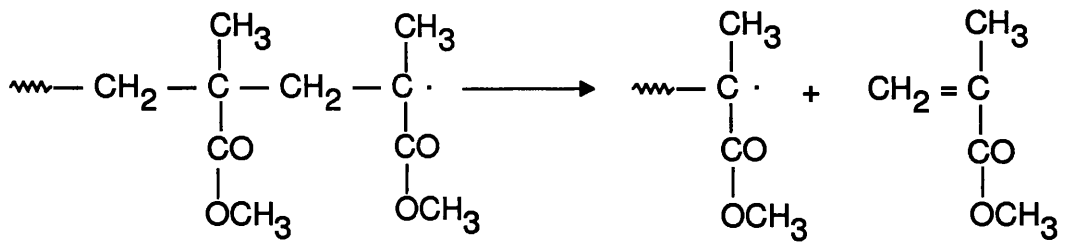


Fig. 1.1 Depolymerisation of poly(methyl methacrylate)

Grassie and Melville also measured the rates of degradation of poly(methyl methacrylate) at various stages of thermal degradation and found that activation energies increased with extent of degradation. Madorsky (16) and Hart (17) made similar studies on PMMA and obtained results in agreement with those of Grassie and Melville.

Non-Radical depolymerisation

Poly(dimethyl siloxane) is one among few examples of non-radical depolymerisation. Poly(dimethyl siloxane) produces a whole range of cyclic oligomers from trimer to at least heptadecamer on thermal degradation (7). The polysiloxanes are generally terminated by hydroxyl groups, which are known to play some part in the degradation reaction as replacement of them with trimethylsilane groups increases the stability of the polymer while the addition of potassium hydroxide decreases the stability of the polymer. The reaction mechanism for the formation of the trimer is given in Fig. 1.2. The reaction of the hydroxyl group at point further from the chain end will lead to higher oiligomers.

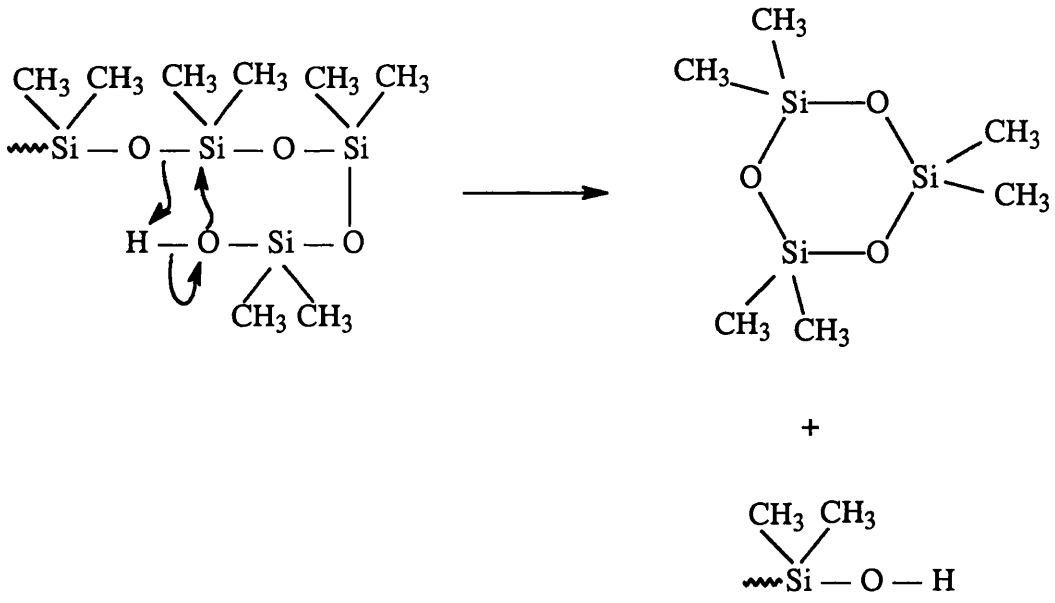


Fig. 1.2 Mechanism of degradation of poly(dimethyl siloxane)

In some cases it is difficult to determine the nature of the depolymerisation. For example a widely accepted view is that the depolymerisation of poly(ehtylene terephthalate) (PET) is of the non-radical type depolymerisation (18). In this case it has been suggested that the initial breakdown of PET is through a primary alkyl-oxygen scission of the β—hydrogen type. This reaction is facilitated by the possibility of forming a six-membered ring transition state (Fig. 1.3).

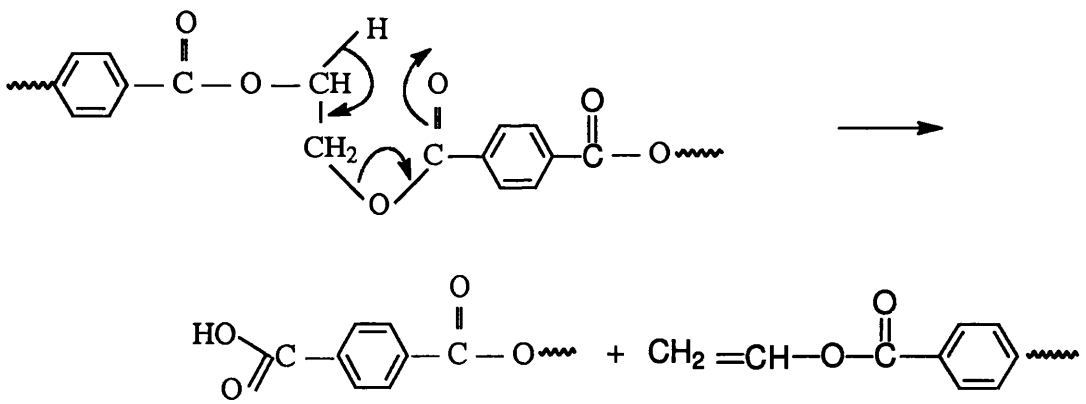


Fig. 1.3 Initial decomposition proposed for poly(ethylene terephalate) (ref 18)

However during the thermal degradation of (PET) the continuous formation CO and CO_2 has been observed by McNeill & Bounekhel (19). The continuous formation of CO and CO_2 is difficult to explain by a non-radical depolymerisation reaction. Hence McNeill & Bounekhel proposed that scissions occur homolytically which can easily account for these and other observed products (Fig. 1.4).

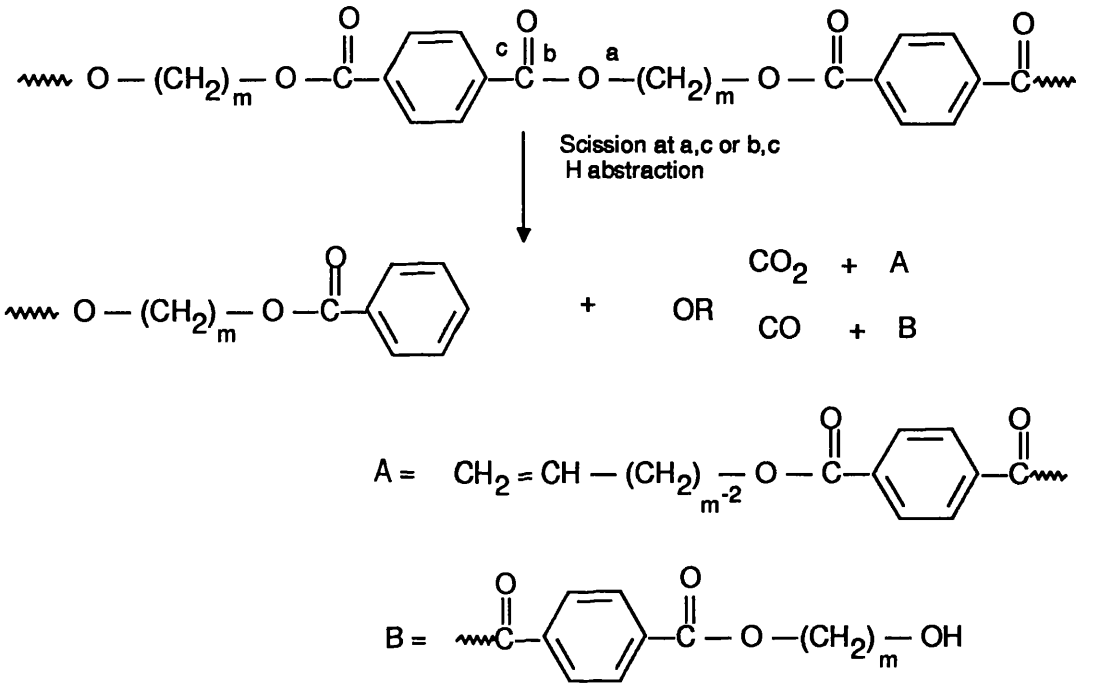


Fig. 1.4 Radical mechanism proposed for poly(ethylene terephathalate)

Side Group (Substituent) Reactions

Side group reactions degrade the polymer by reaction of the substituents, but not through the breakdown of the main chain. They depend predominantly upon the chemical nature of the side groups on the polymer backbone and usually occur at relatively lower temperatures than those at which main chain bonds are broken.

These reactions may be free radical, molecular or ionic in nature and can be sub-divided into three main types.

(a) Elimination

(b) Ester decomposition

(c) Cyclisation

Elimination

Typical examples of elimination reactions are those occurring in degradation of poly(vinyl chloride) (PVC) and poly(vinyl acetate) (PVA).

PVC degrades around at 200°C eliminating hydrogen chloride and forming a coloured highly conjugated residue (Fig. 1.3) (20,21). The role of hydrogen chloride in the degradation of PVC has caused a great deal of controversy, despite the efforts of countless investigators over many years. It has been suggested that the process is ionic (22), radical (23) or more recently a molecular or concerted mechanism has also been suggested (24). It seems however that a free radical path must play an important role in the degradation of PVC.

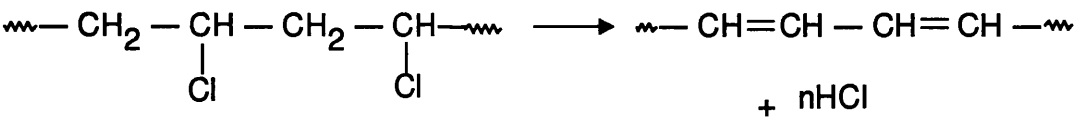


Fig. 1.3 Elimination reaction in PVC

PVA was first studied in detail by Grassie, (25) who found that this polymer is slightly more stable then PVC, but degrades in similar fashion. Later studies (26,27) have reported that PVA eliminates most of the acetate

groups as acetic acid at moderate temperature. This results the formation of double bonds, which accumulate and generate aromatic rings through Diel-Alder condensation.

Ester Decomposition

These reactions involve generation of the parent acid together with an olefin, and have been found to take place in some ester polymers as in pyrolysis of small ester molecules. When polyacrylates or polymethacrylates decompose in this way, the olefinic fragment is liberated as a volatile product.

A typical example of this process is given by pyrolysis of poly(tert-butyl methacrylate) which liberate iso-butene leaving poly(methacrylic acid) in the residue (28).

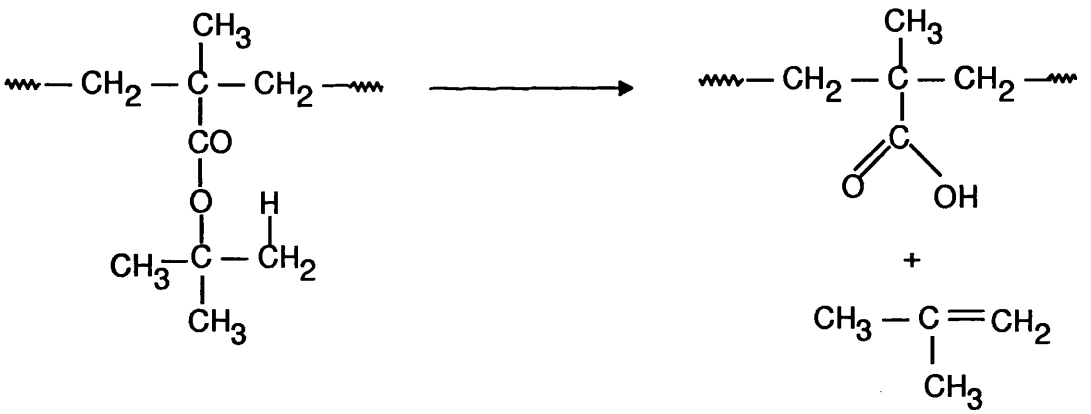


Fig. 1.4 Pyrolysis of poly(tert-butyl methacrylate)

Cyclisation

Intermolecular cyclisation reactions can generally occur in those cases in which substituent groups are potentially reactant at elevated temperature

and are located in the close proximity. This may or may not involve elimination of small molecules.

For example, in polyacrylonitrile the change involves only structural rearrangements and the polymer colours thermally at 175°C due to linkage of nitrile groups to form conjugated carbon-nitrogen sequences, which are similar to those that occur in polymethacrylonitrile (29,30).

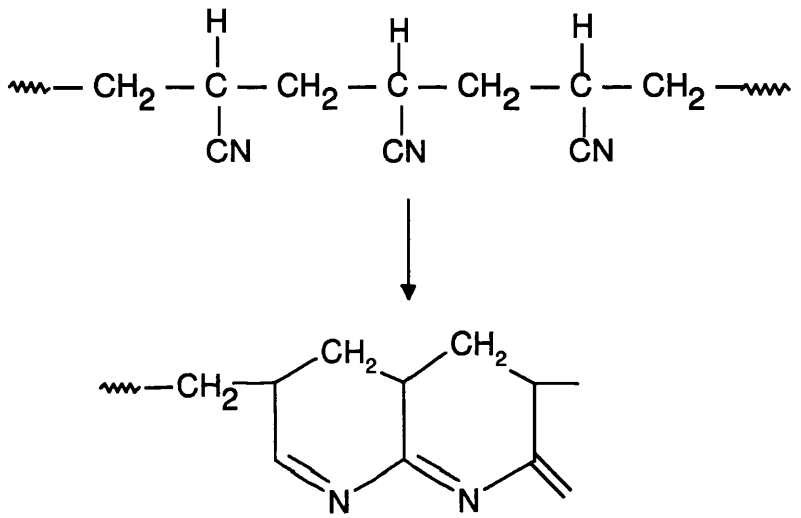


Fig. 1.5 Cyclisation reaction in polyacrylonitrile

In other cases the polymer may undergo a cyclisation reaction with concurrent elimination of a small molecule, as in the case of poly(methacrylic acid) (PMAA) (27) or poly(methyl vinyl ketone) (PMVK) which can undergo random Cyclisation of adjacent monomer units with release of water. (31, 32)

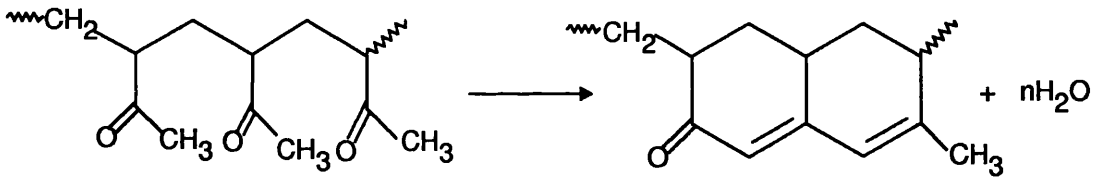


Fig. 1.6 Cyclisation in PMVK

THERMAL DEGRADATION BEHAVIOUR OF ALTERNATING COPOLYMERS

Alternating copolymers have a very different chain structure from the normal random type of copolymers because of strictly ordered sequence of the two types of monomer units. Hence, if the side groups from each co-monomer decompose or react together without backbone scission then it may be possible to make new materials that cannot be synthesised by direct polymerisation.

For example, if one of the co-monomers in an alternating copolymer degrades by side group scission and is thermally less stable than the other, then degrading it at moderate temperature may induce a side group reaction that will leave the backbone intact. This would result in a copolymer with a new backbone structure.

For example, in the case of the maleic anhydride—vinyl acetate copolymer (33), the vinyl acetate units undergo side group scission and abstract a hydrogen from the neighbouring maleic anhydride units around at 200°C before extensive backbone scission occurs. This will lead to the formation of a novel type of polymer structure. This type material has already proved useful as a polymeric encapsulant for slow drug release in the body, because it is possible to control quite precisely from the extent of thermal degradation the ability to take up water. Other applications for such

materials formed by controlled degradation are also possible, such as char forming products to reduce flammability in polymeric composition.

Methods of studying polymer degradation

A variety of methods has been developed in order to investigate the thermal stability of polymers. These methods include the measurement of changes in physical properties as well as chemical changes. The choice of method of evaluation of polymer degradation depends upon the objectives.

In general no single method gives sufficient information, which can give an overall picture of the thermal behaviour of the polymer, so it is necessary to use a number of complementary analysis techniques.

Viscometry, osmometry or gel-permeation chromatography can be used to determine the change in molecular weight distribution of the polymer, while by using infra-red, ultraviolet or NMR spectroscopy, changes in the functional groups in the polymer can be observed.

Today, a variety of commercial instruments are available which allow the elegant investigation of the thermal behaviour of polymers. Among them the most important technique is thermogravimetry (TG), in which loss in weight is measured. Other techniques are differential scanning calorimetry (DSC) and the closely related differential thermal analysis (DTA) in which heat absorption or evolution due to either physical or chemical changes within the polymer are measured.

Thermal volatilisation analysis (TVA) is a generally more applicable technique in which the pressure of volatile degradation products is measured as a function of temperature or time in a continuously evacuated system. Unlike most other thermal analysis methods, in TVA the products of

degradation are immediately available for subsequent analysis. TVA will be discussed in more detail in subsequent chapters.

OBJECTIVES OF THIS WORK

The main objective of this project was to investigate the thermal degradation behaviour of a range of alternating copolymers and the suitable cases to examine the possibility of using controlled degradation as a route to synthesising novel materials.

Controlled degradation has been used previously to make carbon fibres, which have extremely good tensile strength and flame resistant properties. However there has been relatively little research into this type of procedure.

By performing degradation experiments on a several alternating copolymers it was hoped that an understanding of the principles involved could be ascertained and other synthetic pathways could be predicted.

In addition, the experiments have provided a large amount of data on the degradation of the polymers used, which will enable decisions about the suitability of the polymers for whatever commercial reasons e.g. incineration, operating temperatures, flammability etc.

The detailed analysis of degradation products was also the intention, in view of current concern regarding, flammability and possible toxic products released during the incineration of waste.

The thermal stability of the copolymers has also been investigated isothermally at lower temperature with the aim to determine the effect of less thermally stable unit on the thermal behaviour of the alternating copolymer.

CHAPTER TWO

EXPERIMENTAL TECHNIQUES OF POLYMER THERMAL DEGRADATION

A description of the apparatus and techniques employed in the present studies is given in this chapter. Particular emphasis is given to thermal volatilisation analysis (TVA) which is the most versatile of the techniques described and allows study of all the products of degradation.

THERMAL ANALYSIS

INTRODUCTION

Thermal analysis is defined as the group of techniques in which physical properties of a substance are measured as a function of temperature while the substance is subjected to a controlled temperature programme.

When a polymer decomposes, there are different product fractions. The mechanisms of thermal degradation are complex and result in the formation of products with various characteristics. Products may be gases volatile enough to be non-condensable in a liquid nitrogen trap at -196°C, gases and liquids which are volatile at room temperature but condensable at -196°C, tars, waxes, etc, which are volatile at degradation temperature but not at room temperature, or involatile materials.

Various methods of thermal analysis have been developed, and many of them are available commercially. The method of study of thermal degradation of a polymer depends upon the objectives of the investigation of physical phenomena (e.g. change in crystallographic properties, melting, sublimation, absorption or evolution of heat), and chemical phenomena (e.g. degradation, decomposition, oxidation). The most important and widely applicable techniques are TG, DTA, DSC, and TVA.

THERMAL VOLATILISATION ANALYSIS (TVA)

TVA is now a well established technique of thermal analysis and has been the subject of a number of publications (34-39). As TVA was widely used in studying the thermal degradation behaviour of many polymers it is desirable to give a full description of the apparatus and its operation.

PRINCIPLES OF TVA

TVA involves the continuous measurement of the pressure exerted by the volatile products as they are evolved from the heated polymer sample. Degradation is carried out under high vacuum conditions and the volatile products are thus continuously pumped from the heated sample. The volatiles pass to a cold trap and the response of a Pirani gauge placed between sample and trap is recorded continuously as a function of oven temperature. The Pirani response is a measure of the rate of the volatilisation of the sample (Fig. 2.1).

In TVA the cold trap is kept at -196°C by cooling with liquid nitrogen. This is sufficient to condense all the commonly found products of polymer degradation except gases such as carbon monoxide, hydrogen and methane. As a result of this, the liquid nitrogen trap acts as a pump for most of the evolved products if the system is evacuated before degradation begins and variation in the pumping speed in different systems is of minor importance.

DIFFERENTIAL CONDENSATION TVA

The TVA technique can be modified (38,39) by placing an additional trap before the Pirani gauge at a temperature higher than that of the original trap, as shown in Fig. 2.2. By varying the temperature of this trap, an indication of the range of volatility of degradation products can be gained, by comparing the change in pressure reading obtained as the temperature of the trap is altered.

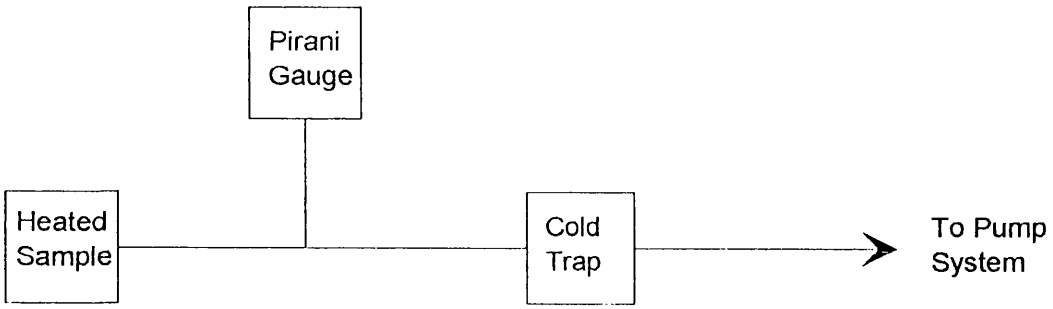
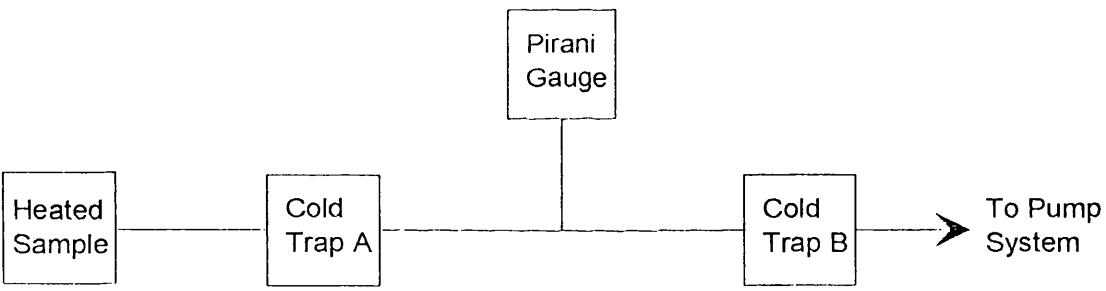


Fig. 2.1 Basic TVA system



Temp A > Temp B

Fig. 2.2 Differential Condensation TVA system

The form of apparatus currently used in the present work is illustrated in Fig. 2.3. In this, the vacuum system is split into four separate parallel limbs each with an initial trap and a main trap (-196°C). The product stream may pass through each limb which operates usually with different initial trap temperatures, 0°C, -45°C, -75°C, and -100°C, respectively.

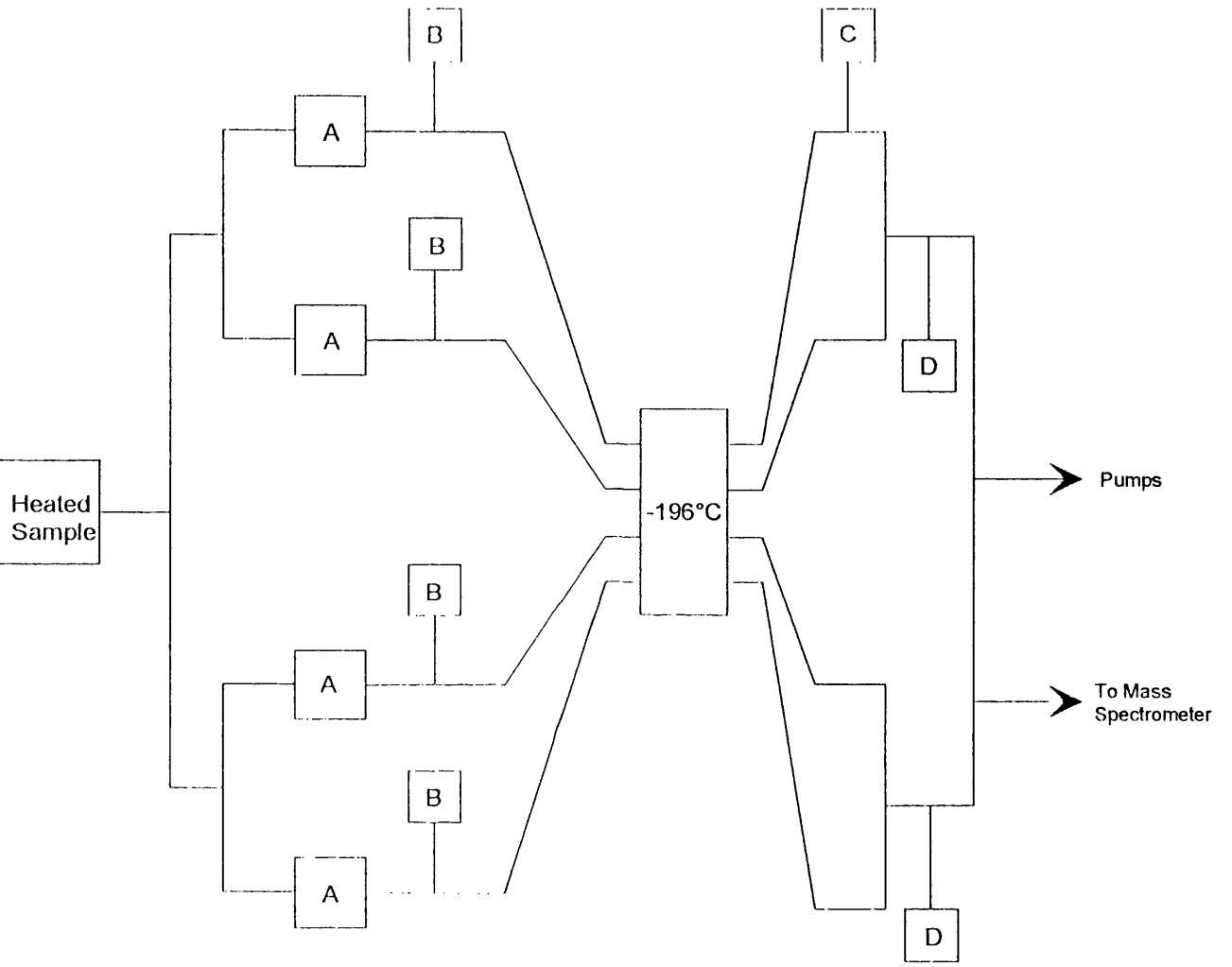
A Pirani gauge is positioned between each of the initial traps and the liquid nitrogen trap, and the fifth Pirani gauge is placed after the liquid nitrogen traps (-196°C), to monitor the non-condensable gases evolved. An on-line mass Leda-Mass quadrupole spectrometer is used to identify the non-condensable gases produced.

TVA IN PRACTICE

In the TVA system, it is desirable that the polymer sample used should be in the form of a thin film or finely ground powder. If the sample is too thick the degradation rate could be affected by the rate of diffusion of volatilies out of the polymer, or the degradation products could undergo secondary reactions giving misleading information about the reaction mechanism.

A diagrammatic representation of the oven and the degradation assembly of a typical TVA line is shown in Fig. 2.4. A Perken Elmer F-11 gas chromatography oven has been modified to take the tube assembly and to work to a maximum temperature of approximately 500°C. The oven can be used isothermally, or by using a programming module, which provides a linear temperature increase. Most of the TVA work for this research was carried out in programmed heating mode, using a heating rate of 10°C/min. The temperature in the oven was recorded by a K-type nickel-chromium/nickel-aluminium thermocouple, placed in the oven as close to the bottom of the sample tube as possible.

The polymer sample is degraded in a tube made from Pyrex glass, fitted with a B40 cone, for connection to the vacuum line, 25 cm in length and 3.5 cm diameter, giving a flat and an internal base area of approximately 9 cm^2. Water cooled condensers are placed either around the outside or inside the



A = 0°C, -45°C, -75°C, -100°C traps
B, C = Pirani gauges
D = Sample take off points

Fig. 2.3 Parallel Limb Differential Condensation TVA System

tube to condense the products volatile under vacuum at the elevated temperatures but not volatile at room temperature. These products are called the cold ring fraction.

The system is evacuated prior to use down to a pressure of 10^{-4} torr, and is continuously evacuated during the experiment. The pump system used was an Edwards Speedivac ED100 oil diffusion pump backed up by an Edwards Speedivac 25C20A oil rotary pump. Pressure were measured using Edwards PRL 10 Pirani gauge heads with Pirani 1001 meter units.

Pirani gauge output is dependent on the nature of the gas as well as the absolute pressures, so that for quantitative analysis of degradation products calibration curves must be constructed.

The following designation for the individual trap traces of TVA curves is employed in this work as standard.

————	0°C	(and colder traps if coincident)
.....	-45°C	
----------	-75°C	
_ _ _ _ _ _	-100°C	
— · — · — · —	-196°C	

By means of a system with various cold traps at temperatures from 0° to -196°C preceding Pirani pressure gauges a considerable amount of information about product volatility and changes in product composition during the heating programme may be collected in a single TVA experiment. In addition to these data the number of stages of breakdown and their threshold and maximum rate temperatures can also be obtained (6).

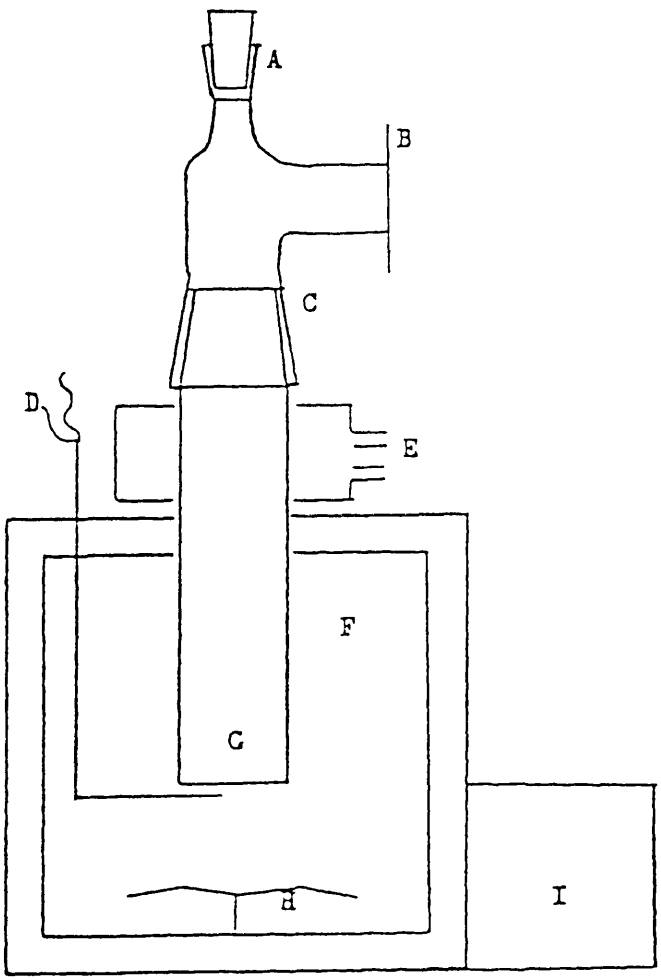


Fig. 2.4 Oven and Degradation Tube Assembly

A = B19 socket

B = Ground glass flange joint

C = B40 ground glass joint

D = Type K thermocouple

E = Water cooled jacket "cold ring"

F = Oven

G = Degradation tube

H = Fan

I = Programming module

When only totally volatile products and total -196°C non-condensable products are recorded, the designation is as follows,

_____ Total volatile products

— · — · — · — Total -196°C (non-condensable products)

TEMPERATURE CALIBRATION

The temperature recorded during an experiment is that of the fixed thermocouple as shown in Fig. 2.5. This is always higher than the actual sample temperature of the interior of the base of the degradation tube due to the temperature differential across the tube base.

To overcome these difficulties, the difference in temperature between the oven thermocouple and the bottom of the inside of the tube is measured by placing another K-type thermocouple inside the sample tube and recording the output of both thermocouples as the oven temperature is raised.

This has to be repeated for each sample tube to allow for any difference in the size, or the thickness of glass used in the tubes, or if the position relative to the thermocouple is changed. The temperatures quoted in the results have been adjusted to account for the results obtained in the calibration experiment.

LIMITATIONS OF TVA

In TVA, only those products which are sufficiently volatile to reach the Pirani filament are recorded. This means that the Pirani gauge will not detect any change in the system if the products are not volatile enough to reach the Pirani filament.

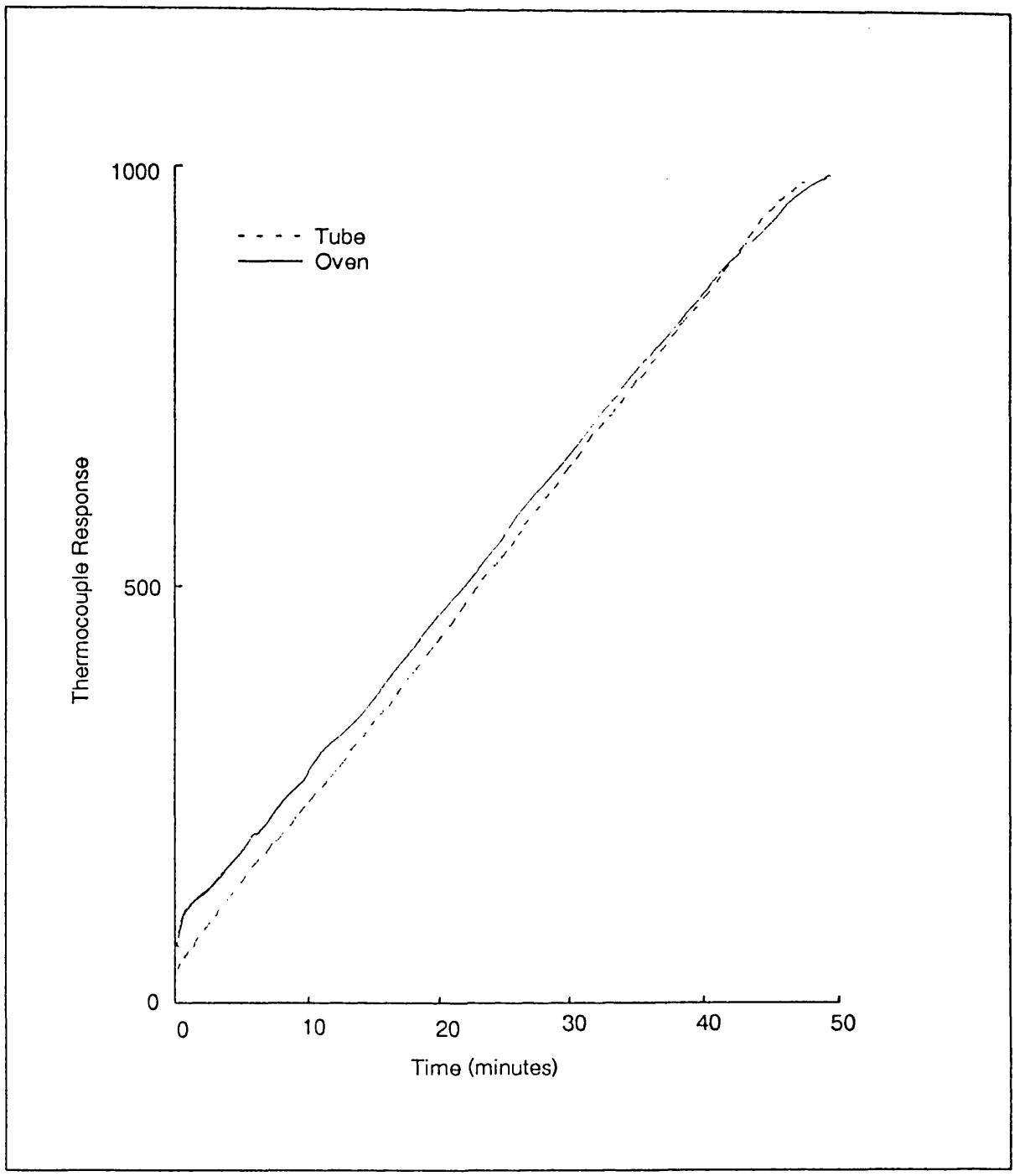


Fig. 2.5 Tube Temperature Calibration Chart

TVA will not give any direct information about any changes to the physical properties of a polymer or structural changes in the polymer as it is being heated. TVA is used in conjunction with other analytical techniques to provide information about the processes taking place as the polymer is being heated.

PRODUCT ANALYSIS

The products obtained from degradation of the sample in the TVA apparatus can be first classified as volatile products and involatile residue. The latter may be examined either at the end of an experiment, or at various intervals by interrupting the run. Infra-red or ultraviolet spectroscopy may be applied to determine the nature of the functional groups present and if soluble, the residue can be subjected to the molecular weight determination.

Volatile products can be further divided into three classes:

a: Tar/wax products which are volatile at the degradation temperature but involatile at ambient temperature. These collected at the top of the degradation tube in the region cooled by the water jacket. Consequently this type of product is referred to as the cold ring fraction (CRF). The cold ring fraction can be removed from analysis either by swabbing with a tissue soaked in a suitable solvent or by scraping with a spatula.

b: Products volatile at degradation and ambient temperature but condensable at -196°C, are called condensables. These can be distilled from the cold trap into a suitable collection vessel (attached at point D in Fig. 2.3) for analysis by infra-red spectroscopy, mass spectroscopy or gas chromatography. A mixture of condensable products is usually first fractionated by means of sub-ambient TVA (which will be described in detail in a subsequent section). The collected volatile products can be separated by controlled warming from -196°C to ambient temperature of the trap containing the products, using the pressure gauges of the TVA system to monitor the volatilisation of each substance.

c: The products volatile at liquid nitrogen temperature (-196°C) are called non-condensable gases. Typically these are hydrogen, carbon monoxide and methane. The non-condensables are pumped through the cold trap system under the continuous pumping conditions of TVA system. These can be identified using an alternative closed system, which consists of an IR gas cell and a cold trap to condense the less volatile substances. Such a typical system has been described by McNeill and Neil (40). In the present studies, a quadrupole mass spectrometer was fitted on the TVA line between the main trap and the pumping system (at point D in Fig. 2.3) and the non-condensables were allowed to bleed into the mass spectrometer at this point.

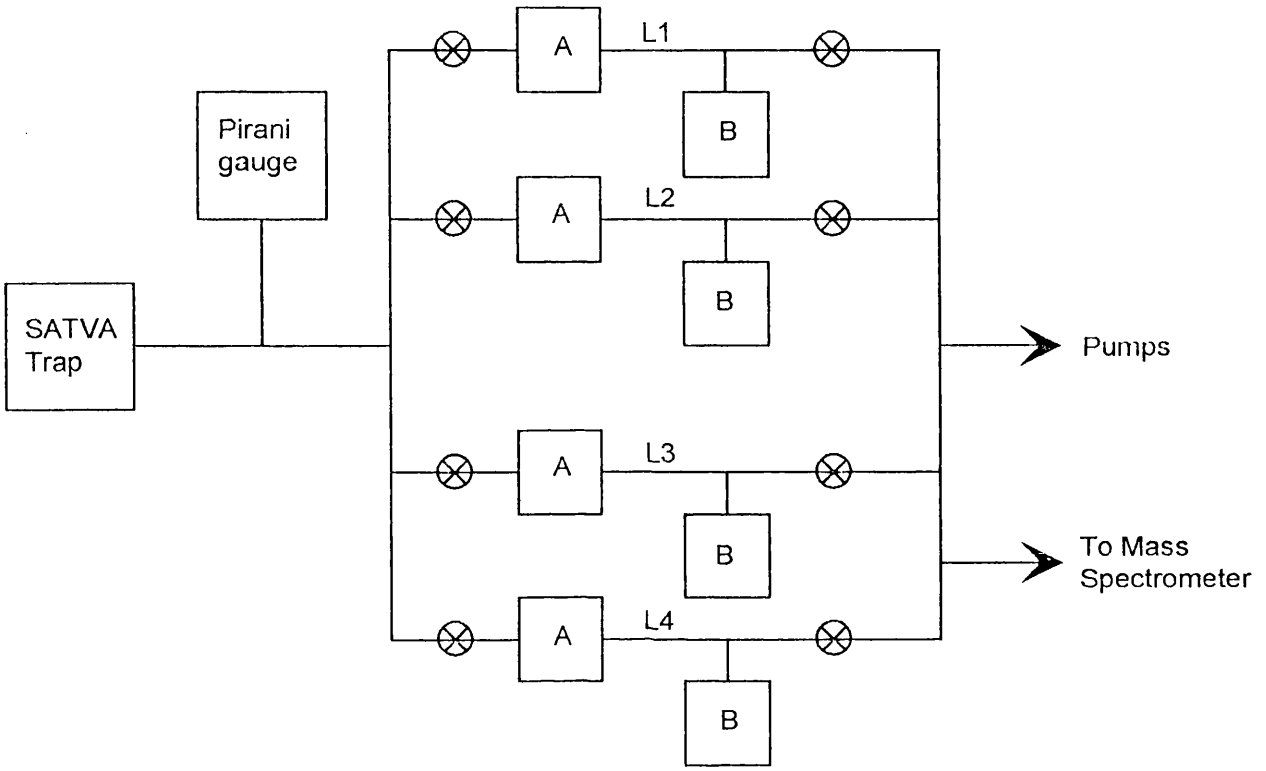
SUB-AMBIENT THERMAL VOLATILISATION ANALYSIS

At the end of a TVA experiment, the various products from the degradation of the sample, except for the non-condensable gases at (-196°C) are present condensed in cold traps in the vacuum system, from which they can be separated for analysis. To be able to elucidate a mechanism explanation for the degradation process it is first necessary to identify the products of degradation.

The technique of sub-ambient thermal volatilisation analysis (SATVA) was developed by McNeill (41), and Ackermann and McGill (42-44) to help in separation, collection and identification of the degradation products.

Before a SATVA separation, the degradation products from the TVA experiment are transferred to a single liquid nitrogen trap cooled to -196°C. The U- type Pyrex glass vessel containing glass beads as shown in (Fig. 2.7) is referred to as the SATVA trap.

Once the condensable products have been collected and the stopcock has been closed, it is then possible to change the direction of pumping in the system to distil the degradation products back out of the trap in the opposite direction. They can be collected as fractions in the vacuum line used in the TVA experiment.



L1 - L4 = Limbs 1 - 4
A = -196°C Trap
B = Take off point

Fig. 2.6 SATVA System

Removal of the liquid nitrogen surrounding the trap, which is kept constantly under vacuum, results in a controlled slow warming up to ambient temperature, because of the surrounding glass beads. In general, longer warming up times enhance the resolution of the peaks, however in some cases peak overlap is unavoidable. The evolution of volatiles is monitored by the Pirani gauge and the readout of pressure within the system can be used as a guide in separating the various products. Mass spectroscopic analysis can also be carried out by bleeding the evolved products as the temperature warms up gradually to 0°C into the mass spectrometer coupled to the TVA system.

The products can be isolated into fractions in different limbs by the successive opening and shutting of the pairs of taps on the vacuum line as shown in (Fig. 2.6), where they are collected for analysis in liquid nitrogen cooled traps.

Once the products have been isolated, they may be removed for analysis by distilling the material from the -196°C trap to an evacuated sample collection vessel. Generally more volatile compounds are distilled into gas cells (Fig. 2.8) and their infra-red spectra recorded. The results obtained can be combined with the mass spectrometry results for identification purposes.

The less volatile products, which are less likely to separate completely, are usually distilled into a liquid finger (Fig. 2.9), from where they can be extracted and identified by IR spectroscopy and GC-MS techniques.

THERMOGRAVIMETRY

The thermal stability of polymeric materials is most widely determined the thermogravimetry (TG). The conclusions drawn with regard to stability are only relevant within the context of loss of weight of the sample. There are, however, reactions which can take place on heating a polymer and which drastically alter the physical properties of the material without an observed change in weight (45).

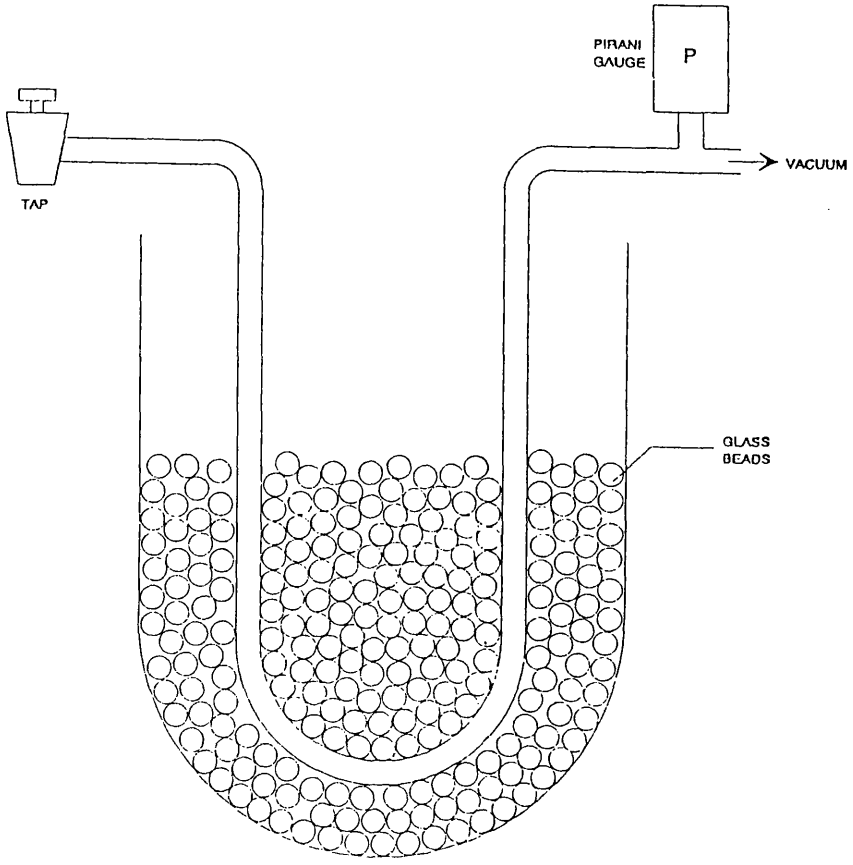


Fig. 2.7 SATVA Trap

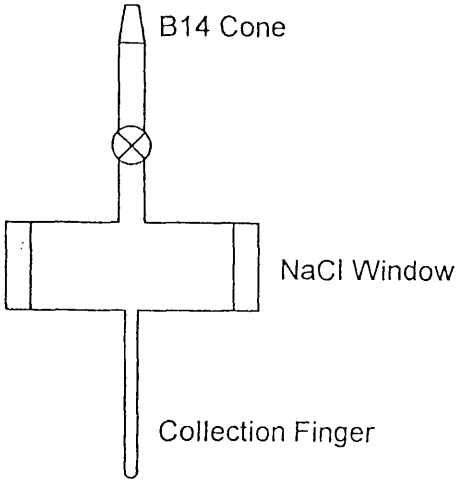


Fig. 2.8 Gas cell

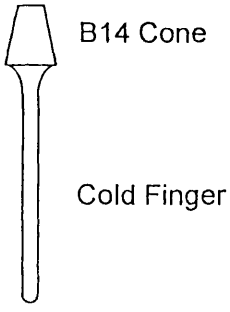


Fig. 2.9 Cold Finger

TG is an important technique which allows a polymer sample to be raised from ambient temperature to as high as 1500°C, while weight loss is recorded directly as a function of temperature. Commercially available equipment for operation to 1000°C (46) and to 1500°C (47) have been described. TG has been used (48) for gas and solid interaction studies to 1600°C. TG has also been coupled to a quadrupole mass spectrometer in a number of systems. (49-52). Simultaneous DTA and TG equipment for operation to 1500°C has been coupled to a quadrupole mass spectrometer.

In the present research a DU Pont 990 Thermogravimetric Analyser was used. The sample was placed in a boat shaped platinum pan hung on a silica rod balance. The weight of the sample was measured under dynamic nitrogen flow (70 ml/min) at heating rate of 10°C/min from ambient to 500°C . Isothermal conditions were also employed in some experiments.

A plot of sample weight remaining as a function of temperature was obtained.

Differential thermogravimetric (DTG) curves were also recorded, which show function the rate of the weight loss in the sample with respect to temperature.

The observations obtained from the TG are in agreement in most cases with data obtained from TVA, although because of the different conditions used, these techniques are not strictly comparable. Differences are most commonly noted when a sample evolves cold ring products, which are recorded by TG but not by the Pirani gauges of the TVA system. The comparison can therefore be instructive.

DIFFERENTIAL SCANNING CALORIMETRY

Differential scanning calorimetry (DSC) is a technique very similar to DTA which measures the effects due to the heat evolved or absorbed by the polymer as its temperature is raised.

In DSC, individual heaters are located as close as possible to the sample and reference vessels. A temperature difference circuit compares the temperature of the sample and reference and supplies power proportionately to a heater in each sample holder so that their temperatures remain the same, where the sample undergoes a thermal transition. A signal proportional to the difference in power supplied is recorded as a function of temperature. The ordinate of the differential thermogram can be expressed in calories or millicalories.

For this research, DSC analyses were performed on a Du Pont 9900 thermal analyser at a heating rate of 10°C/min under nitrogen flow of 70 ml/min.

ANALYTICAL TECHNIQUES

In conjunction with and in addition to the thermoanalytical techniques employed, a number of other analytical techniques were used in the present work which are mentioned below.

INFRA-RED SPECTROSCOPY

Infra-red spectra were recorded using a Nicolet Magna 550 single beam FTIR spectrometer with a scanning range from 4000 cm^{-1} to 400 cm^{-1} with a resolution of 2 $cm.^{-1}$ The intensity ratios were computed in the absorption mode.

Spectra of polymers, copolymers and involatile residues of degradation were run as KBr discs. Cold ring fraction (CRF) spectra were obtained by dissolution in a suitable solvent and casting a films on sodium chloride (NaCl) plates. Volatile gaseous products of degradation were studied using gas cells equipped with 25 mm NaCl windows as shown in Fig. 2.9.

ELEMENTAL ANALYSIS

The elementary analysis of polymers for carbon and hydrogen was performed using a Carlo Ebra model 1106 Elemental Analyser.

MASS SPECTROMETRY

A modified low resolution Kratos MS 12 mass spectrometer in conjunction with a VG Micromass DS 55 data handling system and a high resolution Kratos MS 9025 mass spectrometer with a micromass DS 90 data handling system were used for identification of degradation products.

A Leda-Mass multiquad quadrupole mass spectrometer, coupled directly to the TVA and SATVA system, was also used to analyse degradation products. Non-condensable gaseous products were analysed by bleeding smaller fractions into the mass spectrometer during the heating process. In addition, during the fractionation of condensable products by SATVA, each material may be bled into the mass spectrometer as it is evolved.

GAS CHROMATOGRAPHY

The liquid fraction obtained from SATVA separation and CRFs obtained from the upper part of the degradation tube were analysed by gas chromatography using a Hewlett-Packard 5880A Gas Chromatograph fitted with a CP Sil 5 CB (Chromatopack) fused silica capillary column (25 m × 0.32 mm I.D × 0.12 μ m) and a flame ionisation detector. Injections were operated in split mode (50:1) and helium was used as a carrier gas with a flow rate of 2 ml/min, respectively. The temperature of the column was programmed from 50°C to 220°C (hold time: 5 min) with a heating rate of 5°C/min for products from SATVA separation. For CRF it was programmed from 80°C (2 min) to 150°C (1min) at a heating rate of 30°C/min and then to 250°C (30 min) at a heating rate of 5°C/min. The products were identified by comparing the retention times with those of standards where possible.

Gas Chromatography-Mass Spectrometry (GC-MS)

GC peak assignments for the condensable degradation products were made mainly by obtaining mass spectra at each peak. A Hewlett-Packard 5971 mass selective detector interfaced to a 5890 series II gas chromatograph and computer (Vectra QS/16s) were used. Separations were effected with an HPI fused silica capillary column (12.5 m × 0.2 mm × 0.33 μm)

temperature programmed from 50°C (5 min hold time) to 220°C of (1 min hold time) at 5°C/min. The Grobtype injector (225°C) was operated in split mode (50:1) and the He carrier gas flow rate was 1 ml/min. Mass spectra (70 eV) were recorded in continuous scanning mode. The concentration of the products in the analysed fraction was determined by integrating the total ion current under the peaks. External standard calibrating solutions of the main compounds in toluene were used to assess the total ion current response factors, which in general were close to unity.

The identification of the MS peaks was made using the NIST/EPA/NIH Mass Spectrum Database and the Eight Peak Index of mass spectra (53).

GEL PERMEATION CHROMATOGRAPHY

The services of the Polymer Supply & Characterisation Centre were used to determine the number-average molecular weight ($\overline{M}_n$) of polymers.

The following conditions and columns were used during gel permeation chromatography (GPC).

Columns	P.L. gel x mixed bed-B, 30 cm, 10 microns.
Solvent	Dimethylformamide with 100 ppm LiBr.
Flow rate	1. 0 ml/min
Temperature	80°C (nominal)
Detector	Refractive index (at 80°C)

CHAPTER THREE

SYNTHESES AND CHARACTERISATION OF SOME ALTERNATING COPOLYMERS AND THEIR RELATED HOMOPOLYMERS

This chapter describes the methods used in the preparation, purification and characterisation of monomers, polymers and copolymers.

These consisted of:

Poly(isopropenyl acetate) (PIPAc)	Methacrylic acid—Vinyl acetate Copolymer (MAA—VA)
Poly(methacrylic acid) (PMAA)	Crotonic acid—Vinyl acetate Copolymer (CA—VA)
Poly(vinyl acetate) (PVA)	Maleic anhydride—Allyl acetate Copolymer (MAn—AllAc)
Maleic anhydride—Isopropenyl acetate Copolymer (MAn—IPAc)	

Most of the polymers have been synthesised through free radical polymerisation using AIBN as initiator, although a sample of low molecular weight, additive free poly(vinyl acetate) (PVA), supplied by (BDH) was also used in various thermal degradation studies.

The first section deals with the purification of the starting materials and the preparation and isolation procedures used in the syntheses of polymers,

whilst the final section of the chapter deals with the composition and characterisation of the various polymers and copolymers.

PURIFICATION OF STARTING MATERIALS

Purification of Initiator

Azoisobutyronitrile (AIBN) (supplier: BDH) was purified by recrystallising twice from absolute methanol, with the solution being filtered hot to remove insoluble decomposition products of the initiator (54). The crystals were filtered off, dried under vacuum and stored in darkness at 0°C.

Solid Monomers

Maleic anhydride (MAn) (supplier: Aldrich Ltd) was purified by recrystallisation from chloroform, the solution being filtered hot to remove the insoluble impurities. The fine crystals were dried under vacuum and then stored over silica gel in a desiccator. Crotonic acid (Hopkin and Williams) was used as supplied.

Liquid Monomers

Vinyl acetate, isopropenyl acetate and allyl acetate monomers (Aldrich Ltd) were purified by distillation under vacuum. These monomers were degassed by repeatedly freezing and thawing them under high vacuum using liquid nitrogen. When distilled, the first and last fractions were discarded, with only the middle fraction kept in a calibrated reservoir for further use in polymerisation.

Methacrylic Acid

Methacrylic acid (Aldrich Ltd) inhibited with 1000 ppm hydroquinone and 250 ppm hydroquinone monomethyl ether, was purified by distillation to remove inhibitor before use.

Distillation was carried out at 60°C under reduced pressure in a 250 ml round bottomed flask. This was fitted with a thermometer, condenser and multi-head receiver, which in turn was connected to the rotary pump as shown in Fig. 3.1. Boiling stones were used to avoid bumping. Only the middle fraction was retained for experimental use.

POLYMERISATION PROCEDURE

The various polymers and copolymers were prepared using the standard procedure for free radical polymerisation.

The polymerisations were carried out in a reaction vessel known as a dilatometer. This is made of Pyrex glass provided with a B14 cone for connection to a vacuum line. It also has a constriction to allow sealing under vacuum when heated with an oxygen flame.

The volume of the dilatometers was calculated by filling with acetone using a burette. They were cleaned with detergent 'Pyroneg', distilled water, analytical grade acetone, and dried by pumping to high vacuum. The dilatometers were also flamed out by gentle heating under vacuum prior to use.

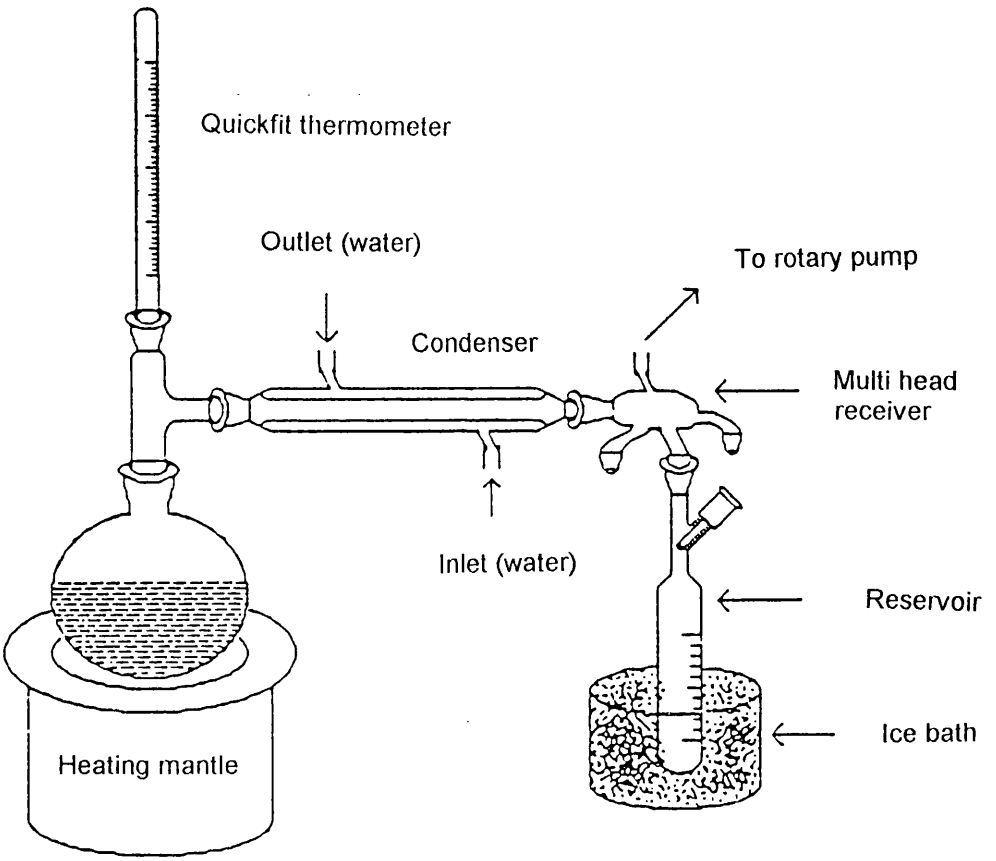


Fig. 3.1 Apparatus for Methacrylic Acid Distillation

Introduction of initiator into dilatometer

To a dilatometer of known volume an appropriate amount of initiator was introduced through a funnel. Any initiator sticking to the funnel stem was washed down with Analar acetone, which was then pumped off under high vacuum.

Introduction of Monomers into dilatometer

The maleic anhydride monomer, which is solid at room temperature, was first dissolved in a calculated amount of Analar acetone and poured into a dilatometer already containing the appropriate amount of purified initiator (AIBN). The mixture (maleic anhydride, acetone and initiator) was degassed to a pressure of 10^{-4} torr and the calculated amount of already purified liquid monomer, such as isopropenyl acetate or allyl acetate, was distilled into the dilatometer. The contents of the dilatometer were degassed again and then sealed off under vacuum.

In the case of crotonic acid/vinyl acetate comonomers, the crotonic acid which is crystalline at room temperature was introduced into a dilatometer containing initiator (AIBN). The contents were then frozen to -196°C and evacuated. After degassing several times, the already purified vinyl acetate monomer was distilled under vacuum into the dilatometer which was then sealed off.

In the case of methacrylic acid/vinyl acetate comonomers, both liquid at room temperature, an appropriate amount of methacrylic acid was poured into the dilatometer containing initiator (AIBN). Then an appropriate amount of vinyl acetate was distilled into the dilatometer and degassed until the pressure was reduced to 10^{-4} torr after which it was sealed. This procedure

was adopted since methacrylic acid cannot easily be distilled due to its low volatility and strong tendency to polymerise when freed from inhibitor.

In the case of homopolymers the appropriate amount of monomers were distilled into the dilatometer containing initiator, then degassed and sealed off under vacuum.

FREE RADICAL POLYMERISATION

The filled dilatometers were warmed up to room temperature for a few minutes to make the reaction mixture homogeneous. The polymerisations were carried out in a constant temperature water bath, the temperature of which was programmable and accurate to ± 0.1°C. The reaction dilatometer was placed in a specially designed glass cylinder coupled to a water bath, in which water was made to circulate from bottom to top and keeping the dilatometer mobile and uniformly warm. The progress of the polymerisation reaction was monitored by observing the fall in the level of reaction liquid in the graduated stem of the dilatometer.

The volume of contraction (Vc) corresponding to extent of polymerisation reaction in any given case was obtained using the Grassie and Vance (55) relationship between contraction and extent of polymerisation in the equation.

$$Vc = V [1 + 0.001 (T - 20)] \%/F$$

where V = Volume of the monomer(s) at 20°C

T = Polymerisation temperature 0°C

% = Extent of polymerisation required

F = % polymerisation/ % contraction

(where F is % change in volume for 100% polymerisation)

The polymersations were conducted to a low conversion, generally less than 10%, except for maleic anhydride—isopropenyl acetate, which had a figure of 18.6%. The polymerisations were kept to a lower conversion to avoid the chances of irregularities in polymer structures. The polymerisation data for various homo- and copolymers are given in Table 3.1.

Table 3.1 Polymerisation Data for Various Polymers and Copolymers

Polymers & Copolymers	Initiator	Temperature of polymerisation	Percentage Conversion
PIPAc*	AIBN	60°C	6.5
PMAA*	AIBN	Ambient	3.5
MAn—IPAc*	AIBN	60°C	18.6
MAA—VA*	AIBN	70°C	3
CA—VA*	AIBN	68°C	5.8
MAn—AllAc*	AIBN	60°C	6.5

* See notations on page 34.

BULK POLYMERISATION

The homopolymer of methacrylic acid was polymerised by bulk polymerisation. The purified monomer was introduced to the dilatometer containing a relatively small amount of initiator (AIBN). The polymerisation reaction was carried out at ambient temperature. This method was adopted because of its great tendency to polymerise when free from inhibitor.

ISOLATION AND PURIFICATION OF HOMOPOLYMERS AND COPOLYMERS

All homopolymers and copolymers were precipitated by pouring the cooled reaction mixture into suitable non-solvents. The precipitate was filtered, re-dissolved into their solvent and precipitated again for further purification. The polymers were finally dried under vacuum at 40°C to constant weight.

Table 3.1 The list of solvents and non-solvents used in purification of various polymers.

Polymers	**Solvent**	**Non-solvent**
PIPAc	Acetone	Ethanol
PMAA	Methanol	Diethyl ether
MAn—IPAc	Acetone	Methanol, ethanol
MAA—VA	Acetone	n -hexane
CA—VA	*	n -hexane
MAn—AllAc	Acetone	n -hexane

* The CA—VA copolymer was thoroughly washed with n-hexane as a suitable solvent could not be found.

COPOLYMER COMPOSITION

The copolymer composition may be calculated by determining the monomer feed for each comonomer using the published reactivity ratios and the copolymer composition equation.

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{(r_1[M_1] + [M_2])}{([M_1] + r_2[M_2])} \quad (3.1)$$

or

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1([M_1]/[M_2]) + 1}{1 + r_2([M_2]/[M_1])} \quad (3.2)$$

Where M_1 and M_2 are the two types of monomers and r_1 and r_2 are their respective reactivity ratios. The reactivity ratio is a measure of the preference for an active centre to add on a monomer of its own type rather than to add on a monomer of the other type. It is calculated by taking the ratio of the rate constant (k) for those two possible reactions.

In the form of equation (3.1) and (3.2), the copolymer composition equation is expressed in terms of molar concentrations of the two monomers, $[M_1]$ and $[M_2]$. However for practical application, it is more convenient to express the equation in terms of mole fractions of one of the monomers.

By defining F_1 and F_2 as the mole fraction of monomers 1 and 2, in the copolymer, and f_1 and f_2 as the mole fraction of the monomers in the monomer feed, the molar proportion of the two monomers at any given instance may be represented as:

$$F_1 = \frac{d[M_1]}{d([M_1]+[M_2])}, \quad F_2 = \frac{d[M_2]}{d([M_1]+[M_2])}, \quad \frac{F_1}{F_2} = \frac{d[M_1]}{d[M_2]} \qquad (3.3)$$

When

$$f_1 = \frac{[M_1]}{[M_1]+[M_2]}, \quad f_2 = \frac{[M_2]}{[M_1]+[M_2]}, \quad \frac{f_1}{f_2} = \frac{[M_1]}{[M_2]} \qquad (3.4)$$

Using (3.3) and (3.4), the copolymer equation can be modified as (3.5) or (3.6)

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \qquad (3.5)$$

$$\frac{F_1}{1-F1} = \frac{r_1 f_1 / (1-f_1) + 1}{1 + r_2 (1-f_1)/ f_1} \qquad (3.6)$$

The values for the reactivity ratios (r_1 and r_2) for various set of comonomers are available (56). The required monomer feed (f_1) for a particular copolymer can be calculated directly from equation (3.5), taking F_1 as the required mole fraction of one of the comonomers in the copolymer.

Monomer feed composition can also be determined from the graph obtained by plotting a series of values of F_1 versus f_1 in equation (3.6). This allows us to estimate the mole fraction of monomer feed (f1) necessary to give a copolymer of required composition.

For random copolymers these graphs take various forms depending on the values of r_1 and r_2. For truly alternating system F_1 is independent of f_1 and

equals 0.5. In some systems, alternating behaviour is formed only over part of the composition range.

The vinyl acetate—crotonic acid (CA—VA) system was synthesised from (1:4) molar ratio of vinyl acetate (VA) (as monomer 1) and crotonic acid to yield 1:1 molar ratio in the copolymer according to the reactivity ratios r_1 = 0.3 and r_2 = 0.01 at 68°C (57). Due to the fact of large difference of reactivity ratios the VA and MAA comonomers, where r_1 = 0.01 (VA) and r_2 = 20 (MAA) do not give totally alternating copolymer. However, the comonomer feeds were chosen using the equation (3.5) which gives a copolymer with a high proportion of alternating sequences.

The F_1 vs f_1 curves for the MAA—VA and VA—CA and systems are reproduced in Figs. 3.2 - 3.3.

The copolymerisation data for various homopolymers and copolymers are listed in Table 3.2.

CHARACTERISATION

All polymers and copolymers were characterised by elemental analysis, infrared spectroscopy and determination of molecular weight.

Molecular Weight Determination

Number-average molecular weight ($\overline{M}_n$) of the various homopolymers and copolymers were obtained using gel permeation chromatography through the services of Polymer Supply and Characterisation Centre, Rapra Technology Limited. The GPC results are summarised in Table 3.3.

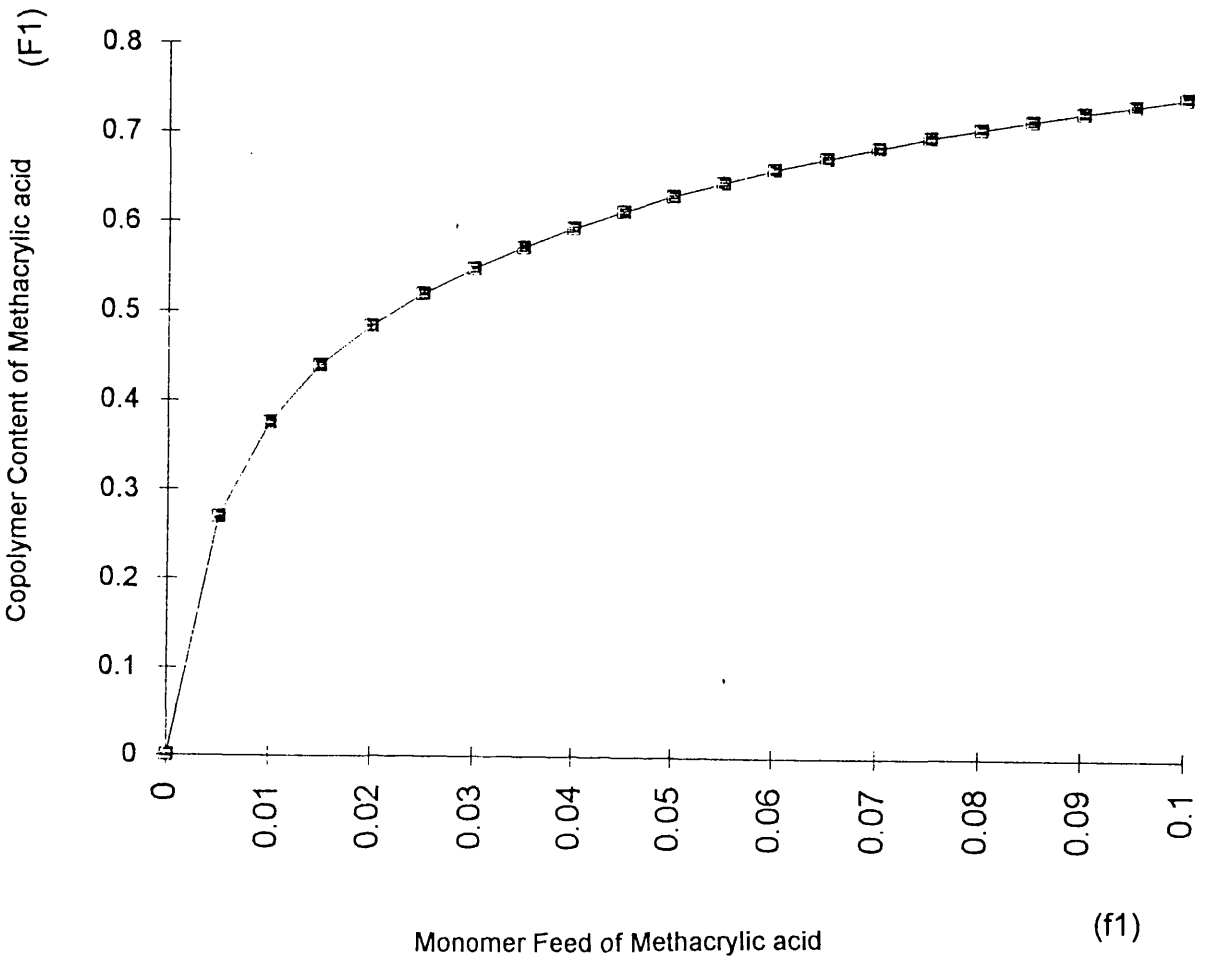


Fig. 3.2 Copolymer Composition Curve for the System

Methacrylic acid - Vinyl acetate

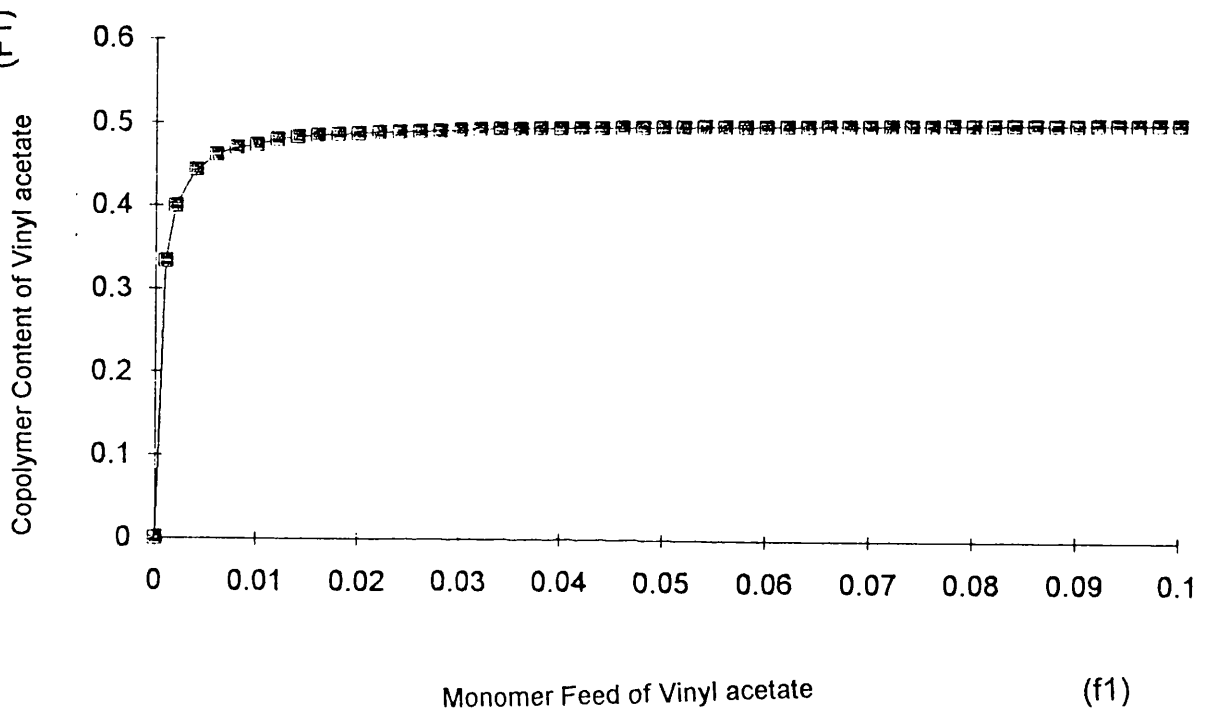


Fig. 3.3 Copolymer Composition Curve for the System

Crotonic acid - Vinyl acetate

Table 3.3 Molecular Weight Data for Various Homopolymers and Copolymers

Polymers & Copolymers	($\overline{M}_n$) by GPC	M_w/M_n
PIPAc	5870	1.424
PMAA	—	—
MAA—VA	17800	1.78
MAn—IPAc	85100	1.72
CA—VA	5200	1.69
MAn—AllAc	98000	1.76

ELEMENTAL ANALYSIS

The elementary analysis of various polymers and copolymer was performed using a Carlo-Erba CHN Elemental Analyser. The percentages of carbon and hydrogen obtained from analysis are listed in Table 3.4. The percentage of oxygen was calculated by difference. The composition of copolymers calculated from the carbon and hydrogen results agreed closely with those calculated on the basis of reactivity ratios.

Table 3. 4 The percentages of C and H of various polymers obtained from elementary analysis.

Polymers & Copolymers	Calculated		Experimental	
	% C	% H	% C	% H
PIPAc	59.98	8.00	59.94	8.00
PMAA	55.81	7.0	53.83	7.84
PVA	55.81	7.0	55.67	7.0
MAn—IPAc	54.54	5.53	54.31	5.41
MAA—VA	55.81	6.97	55.08	6.88
MAn—AllAc	54.54	5.05	53.43	4.90
CA—VA	55.82	7.0	54.71	6.90

INFRARED SPECTROSCOPY

The infrared spectra of polymers and copolymers were recorded using samples in the form of KBr disks. The IR spectra of all monomers were also recorded prior to polymerisation for comparison. The IR spectra of the liquid monomers were obtained by making a sandwich film of monomer between two NaCl salt plates. The spectra of polymers and copolymers are shown in Figs. (3.4 - 3.6).

The IR spectrum of isopropenyl acetate monomer differs from that of the homopolymer in extra bands at 3010, 1640 and 960 cm^{-1}, which are due to ν(=C—H), ν(C=C), and δ(=C—H) respectively, and disappear during the course of polymerisation.

The IR spectrum of poly(methacrylic acid) (Fig. 3.4-b) shows the carbonyl absorption band at 1700 cm^{-1} resulting from hydrogen bond association along with a broad absorption at 3250 cm^{-1} corresponding to ν OH which is characteristic of the COOH dimer. The spectrum also shows a small absorption at 3440 cm^{-1} which corresponds to some water molecules associated with the COOH groups which could not be removed by moderate drying.

The alternating copolymers of maleic anhydride—isopropenyl acetate and maleic anhydride—allyl acetate displayed their characteristic C=O absorptions for anhydride at 1790 and 1854 $cm.^{-1}$ The C=O absorption of an ester is present at around 1740 cm^{-1} in IR spectra of these copolymers. The characteristic bands of all polymers and copolymers are summarised in Table 3.5.

Table 3.5 Assignment of the Principal Peaks Present in the IR Spectra of Polymers and Copolymers.

Infrared band cm^{-1}	Assignment
2990 — 2850	Saturated C—H asymmetric and symmetric stretching for (CH_3) and (CH_2)
1854,, 1794	C=O stretching for cyclic anhydride rings
1735–1750	C=O stretching of ester groups
1700	C=O stretch for COOH groups
1468	CH_2 bending deformation
1440	CH_3 asymmetric bending
1370—1390	CH_3 symmetric bending
1250	(C—O—C) symmetric stretching
1215	distortion or backbone skeleton
1035	(CH—O) symmetric stretching
940—980	CH_3 rocking
735, 605	(O—CO) bending and other deformations

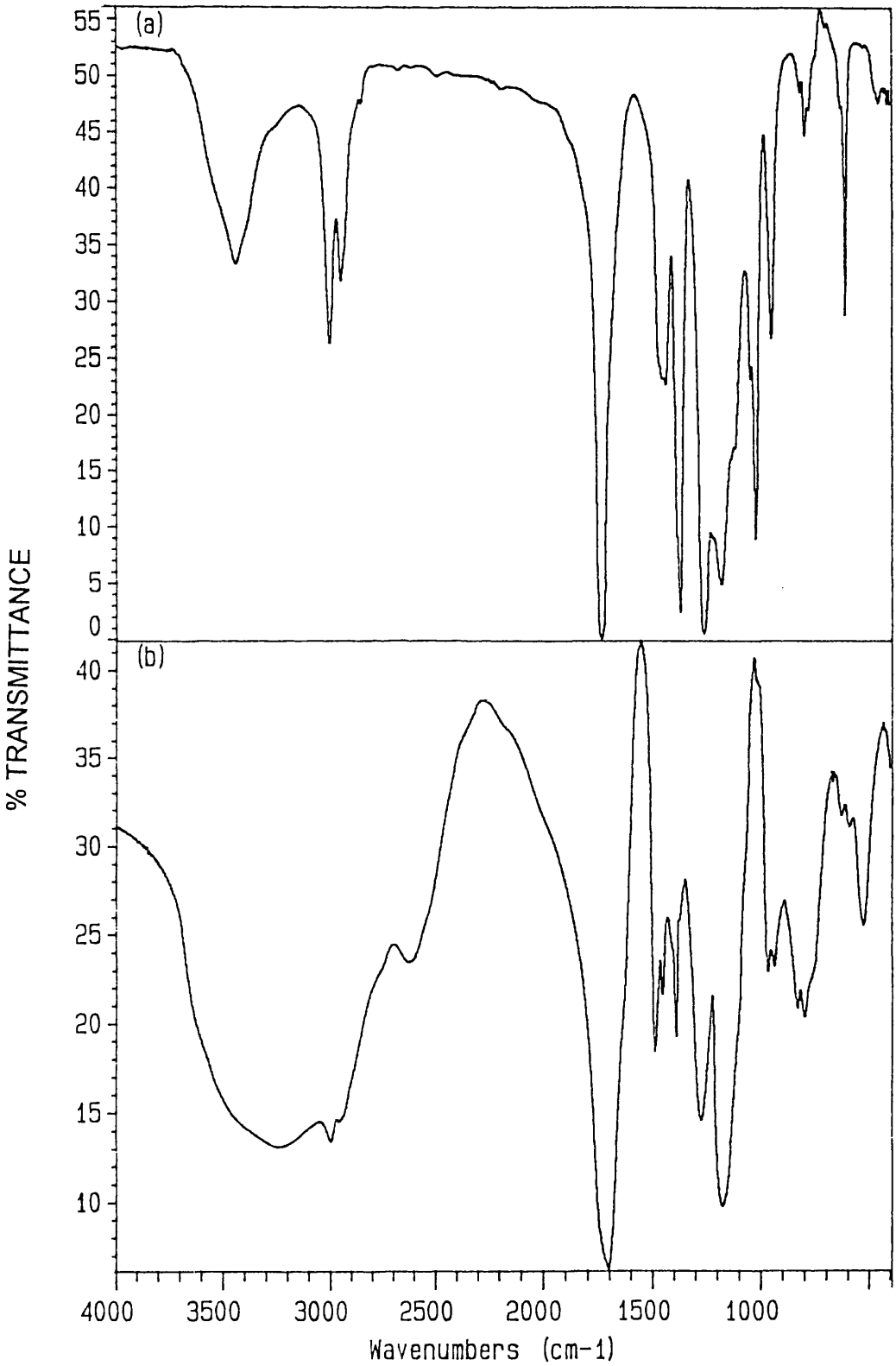


Fig.3.4 FT-IR Spectra of (a) Poly (isopropenyl acetate)
(b) Poly (methacrylic acid)

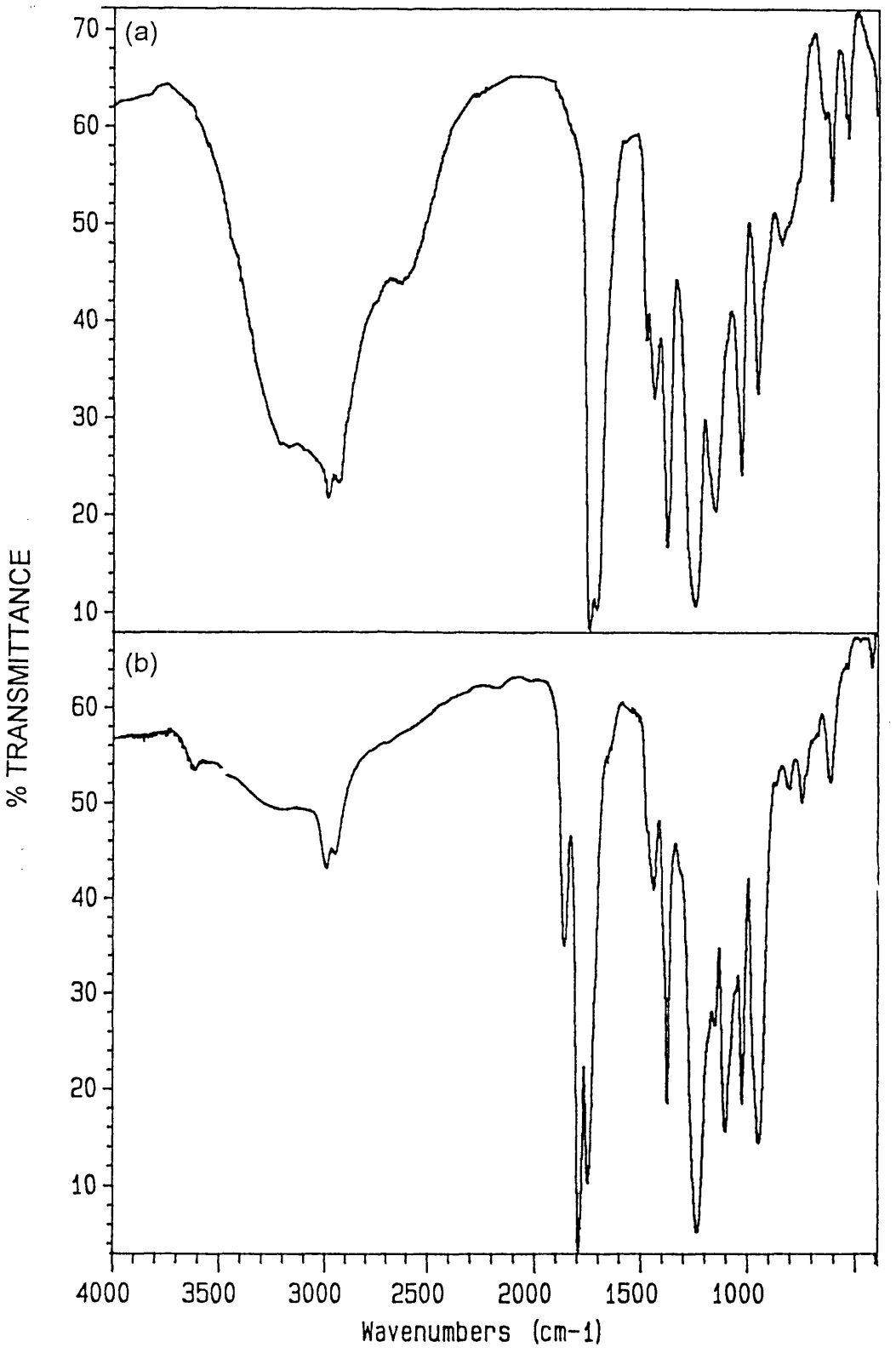


Fig.3.5 FT-IR Spectra of (a) Methacrylic acid—Vinyl acetate Copolymer
(b) Maleic anhydride—Isopropenyl acetate Alternating Copolymer

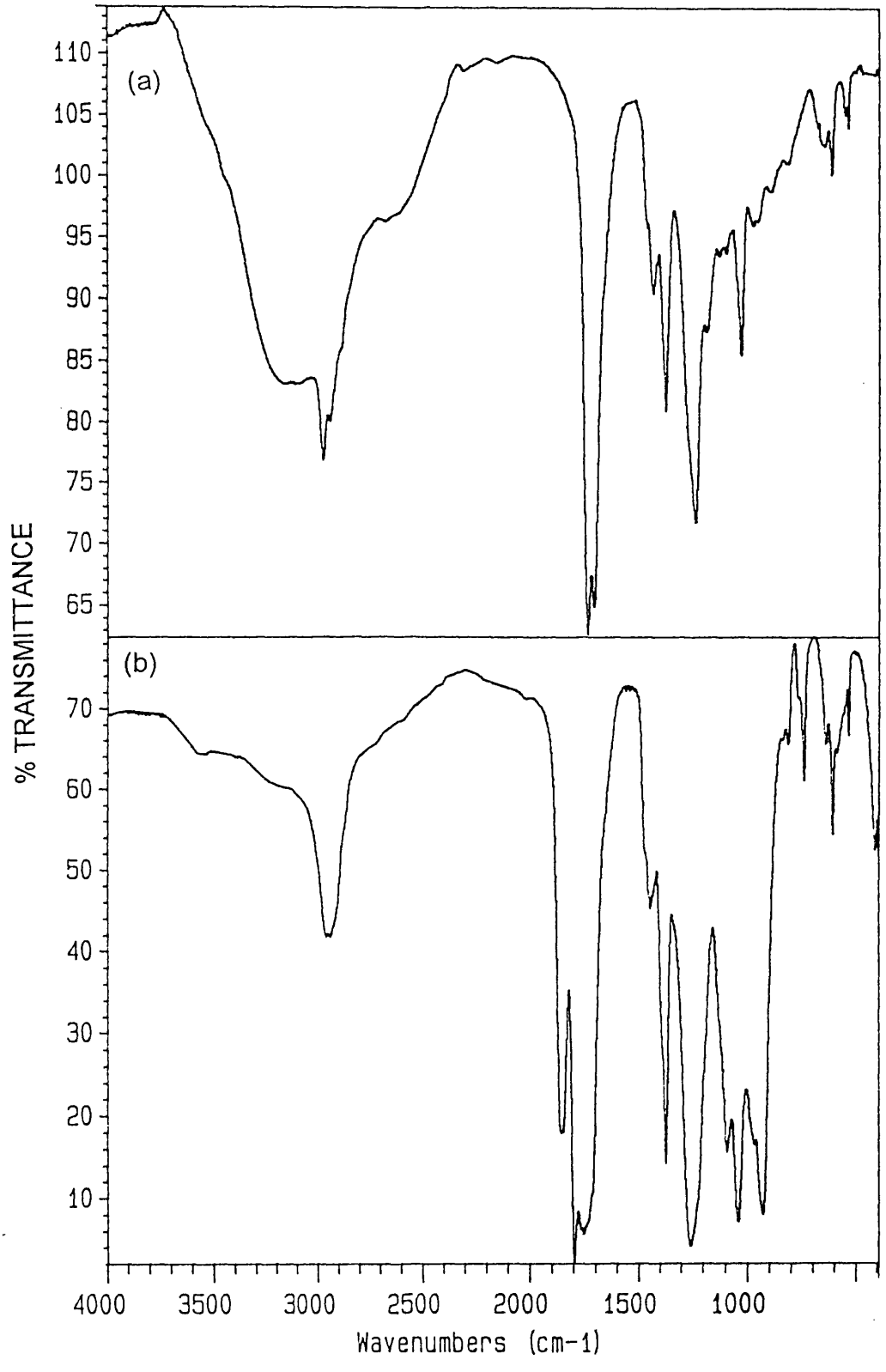


Fig. 3.6 FT-IR Spectra of (a) Crotonic acid—Vinyl acetate Alternating Copolymer (b) Maleic anhydride—Allyl acetate Alternating Copolymer

CHAPTER FOUR

THERMAL DEGRADATION BEHAVIOUR OF POLY (VINYL ACETATE)

INTRODUCTION

The main features of the thermal degradation behaviour of poly(vinyl acetate) (PVA), have been subject of discussion for many years, with certain aspects of the degradation products and mechanism at higher temperature still being undetermined. It is essential to understand the degradation behaviour of PVA as in the following studies the monomer (VA) has been used in various alternating copolymer systems.

PREVIOUS WORK ON THERMAL DEGRADATION OF PVA

Detailed studies of the thermal degradation behaviour of PVA have been carried out by Grassie (25,58). Some other researchers have also been involved in studying various properties of PVA (59,60,61,62,63,64,65).

On heating, PVA degradation is initiated by formation of an acetic acid molecule by decomposition of an acetate side group at a random position on the backbone. This deacetylation can be explained by thermal scission of C-O bonds, as the initial step, occurring randomly along the chain. The C-O bonds are weaker than the C—C bonds so that when polymer is heated these bonds break first, and this process is accompanied by abstraction of hydrogen from an adjacent carbon to form acetic acid and double bond in the chain. This is verified by Servotte and Desreux (59) who have shown that rate of deacetylation is independent of the molecular weight.

After loss of the first acetic acid molecule which is initiated at random, the reaction proceeds along the polymer chain, forming more acetic acid from the side groups in a zipper deacetylation of a short zip length. There is evidence this involves free radical process with $CH_3COO\cdot$ chain carrier (60).

This leads to the formation of conjugated systems giving highly coloured residues and was confirmed by UV spectroscopy by Pavlinee and Kaloforov (61). This has been further explored by Gardner and McNeill (27) who found six or more double bonds in conjugation, less than for degraded poly(vinyl chloride), while Zimmermann (63) detected polyenes with up to twelve conjugated double bonds.

Servotte and Desreux (59) have shown that a cross-linking process co-exists with the deacetylation.

Madorsky (5) has suggested that in some cases abstraction of hydrogen by an acetate free radical may take place intermolecularly, from other chains, resulting in cross-linkages. Pavlinee and Kaloforov (61) have also observed the cross-linking in PVA. These workers have postulated that all the acetate groups have the same reactivity, leading to random loss of acetic acid along the polymer chain.

Other degradation products are formed and can be accounted for through degradation of acetate radical. These include ketene, carbon dioxide and non-condensable gases (H_2, CO and CH_4).

AIM OF THE PRESENT WORK

In the present work, the thermal degradation of poly (vinyl acetate) PVA was followed through the analysis of the evolved volatile products and tar (CRF). The components of the liquid fraction of the polymer have been assessed

and quantitatively analysed by GC-MS. The structural changes in the polymer film were investigated up to the point of charring.

Quantitative measurements of the main product fractions have been made. The gaseous, volatile liquid and cold ring fraction (CRF) products from the TVA degradation have been analysed by IR, MS and GC-MS techniques.

THERMAL DEGRADATION

The thermal degradation behaviour of an additive free sample of PVA (BDH) was examined by well known degradation techniques i.e. Thermogravimetry (TG), Differential Scanning Calorimetry (DSC) and Thermal Volatilisation Analysis (TVA).

THERMOGRAVIMETRY (TG)

The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves for the PVA sample were obtained at a heating rate of 10°C/min up to 500°C under dynamic nitrogen.

The TG curve presented in Fig 4.1 shows that polymer breakdown occurs in two main stages. In the first stage of decomposition, between 250 and 375°C, 70% weight loss is observed. This weight loss corresponds theoretically to the total loss of acetic acid. However the IR spectrum of the partially degraded polymer (66) indicates that a small fraction of acetate groups survive up to 440°C and are gradually converted to α–β unsaturated ketone.

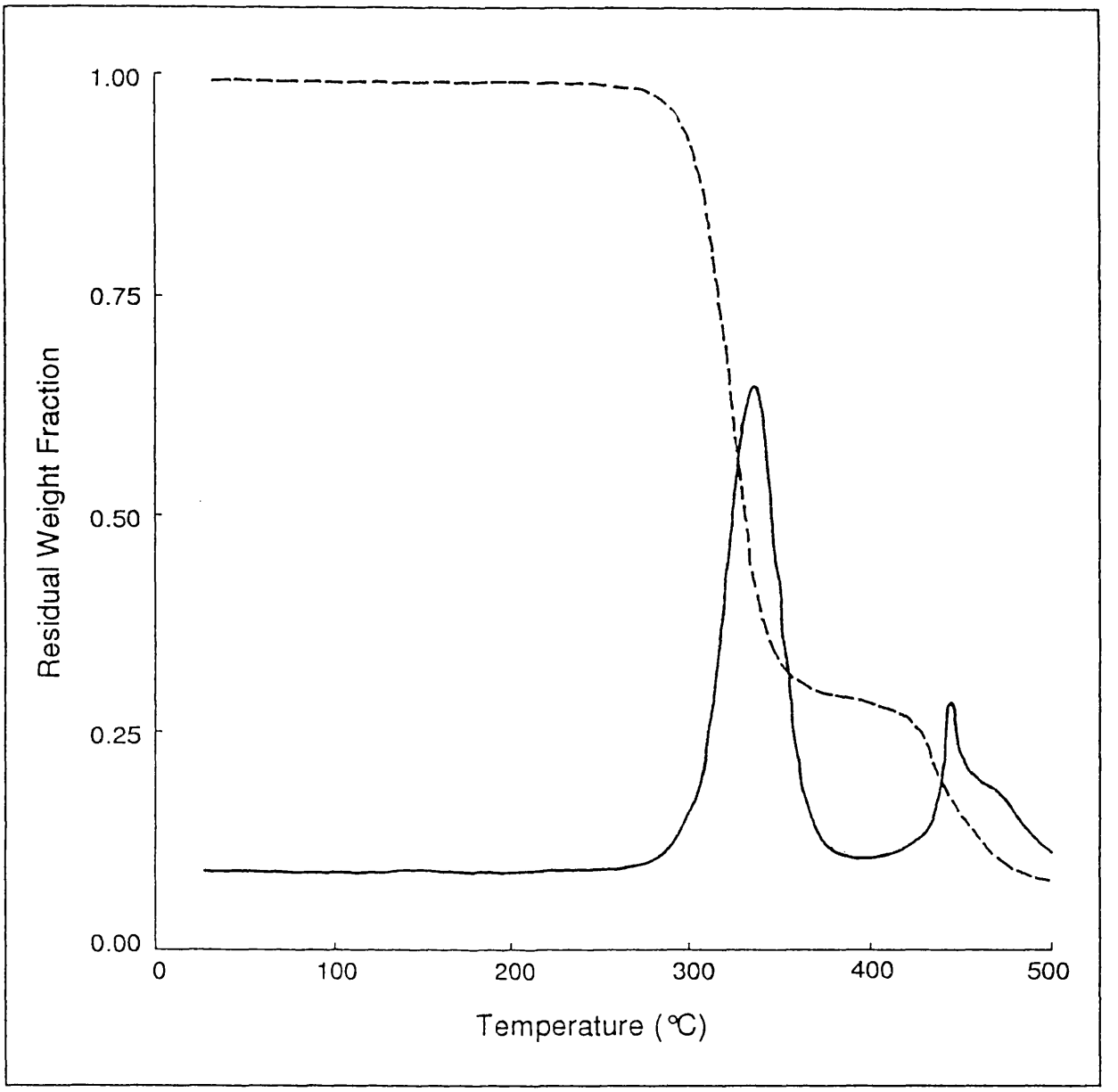


Fig. 4.1 TG and DTG curve obtained (heating rate 10°C/min, nitrogen flow) for PVA sample.

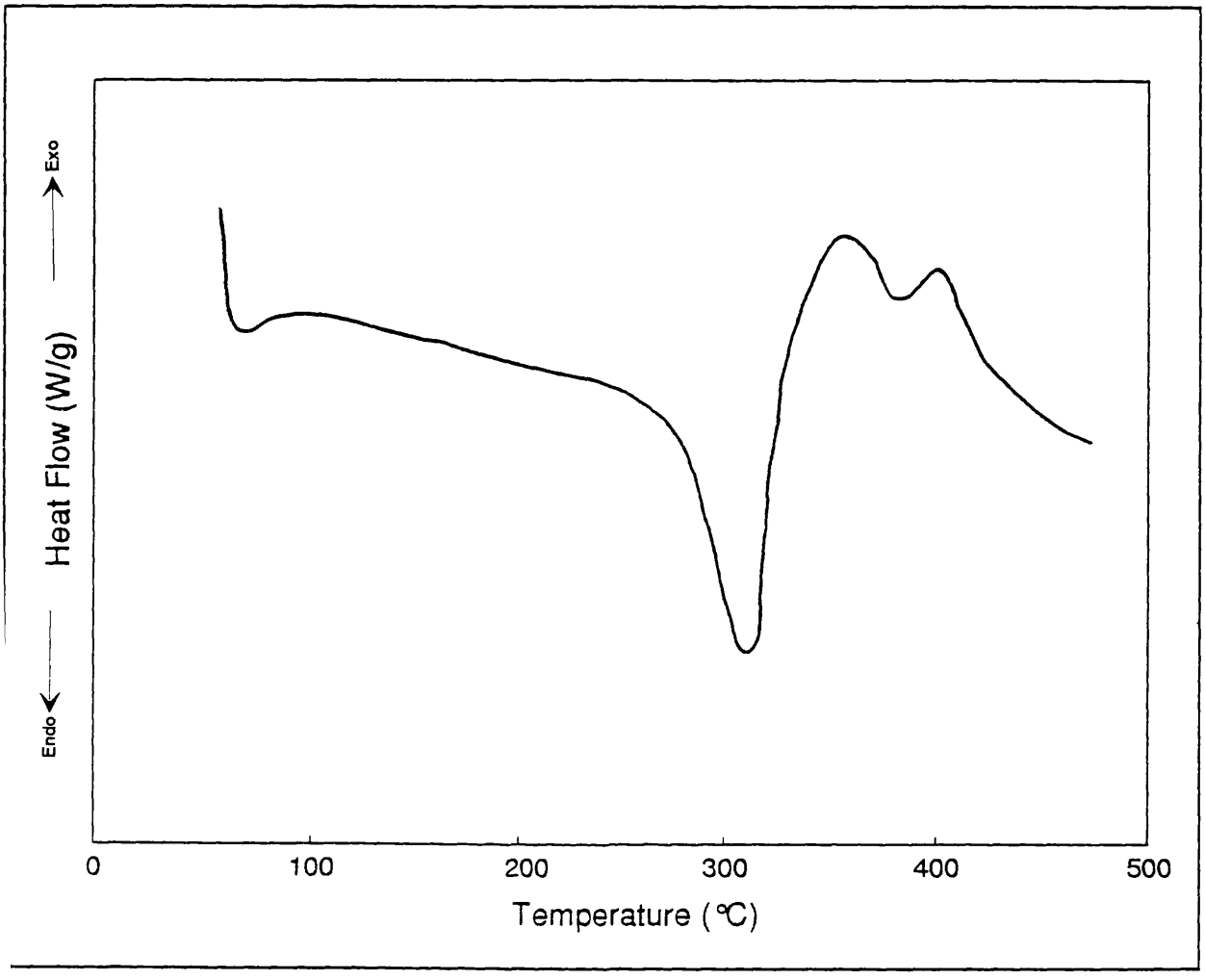


Fig. 4.2 DSC curve for PVA sample obtained at heating rate 10°C/min under nitrogen flow.

The second stage of degradation takes place between 375°C and 500°C and produces considerably less volatile material. The weight loss observed in this stage is only 20%.

PVA leaves 9% residue on heating up to 500°C under dynamic nitrogen.

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

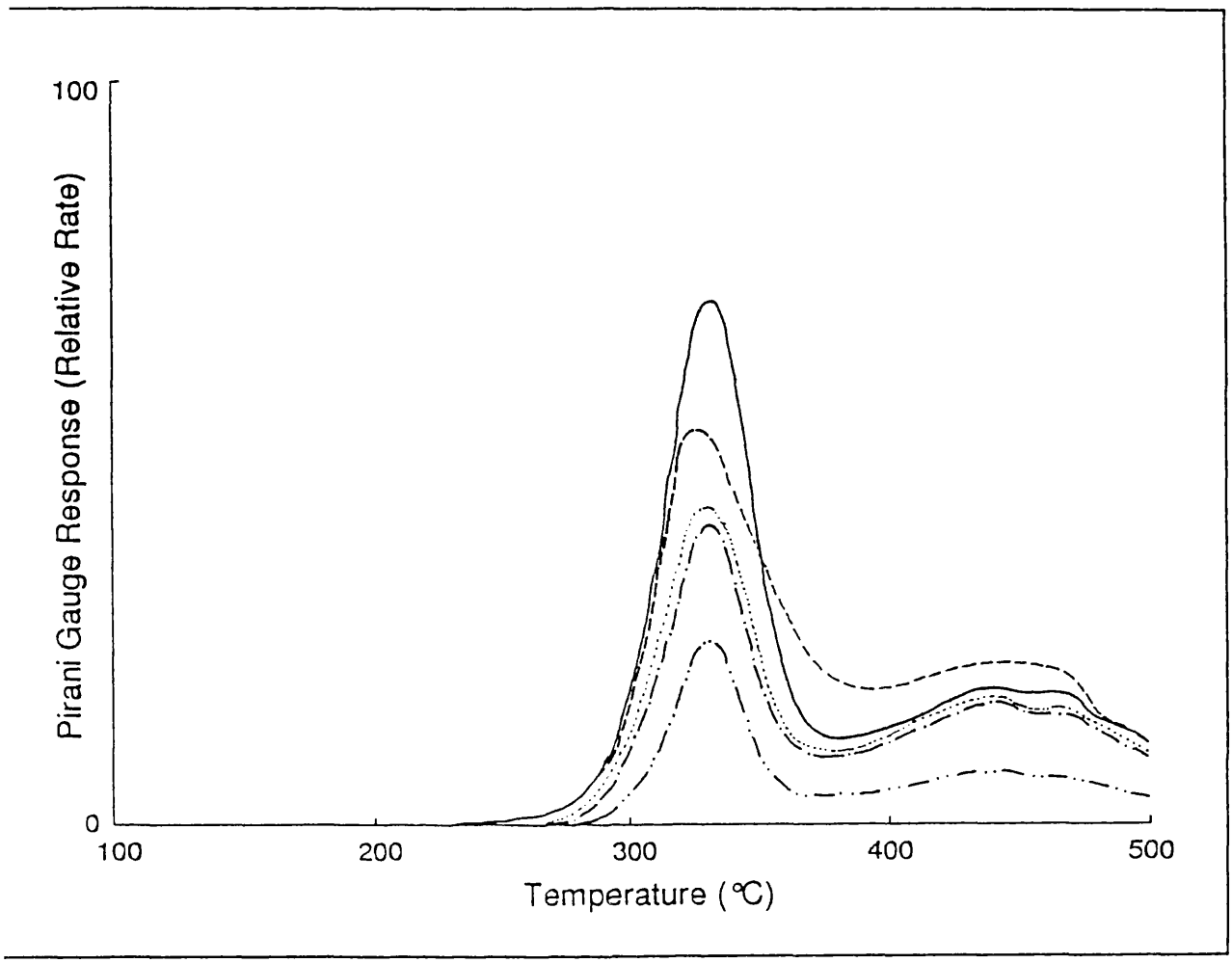
The DSC curve was obtained using heating rate of 10°C/min from ambient to 500°C under dynamic nitrogen flow is presented in Fig. 4.2. This shows a large endotherm in the temperature region 260-372°C. The corresponding enthalpy change is 196 J/g. This large endotherm is associated with the 70% of the weight loss observed in the TG curve.

The DSC curve also shows another endotherm of very small magnitude between 372 and 400°C. The enthalpy change at this stage is only 28 J/g. There is no corresponding endotherm in the DSC curve associated with the second stage observed in the TG curve.

THERMAL VOLATILISATION ANALYSIS (TVA)

The PVA sample, as 60 mg of fine powder, was heated in a TVA system under continuous evacuation to 500°C at 10°C/min. The differential condensation TVA system is described in detail in Chapter 2.

The curve, shown in Fig. 4.3, also shows that PVA decomposes in two main stages.



Key

————	0°C
— — — — —	-45°C
- - - - - - - —	-75°C
— - — - — - —	-100°C
— - - — - - -	-196°C

Fig. 4.3 TVA curve for PVA sample heated in vacuum to 500°C at 10°C/min.

The first stage is between 250 and 375°C with the rate maximum at 325°C. The main product of the first stage is acetic acid, which is completely trapped by the 0 and- 45°C traps, but at - 45°C it condenses and distils over to the liquid nitrogen traps (- 196°C) at a steady rate. This is known as a limiting rate effect (39). In the case of smaller PVA samples, the amount of acetic acid is insufficient for the limiting rate effect, and in such a situation the 0 and -45°C curves become coincident (60).

There are some other products of intermediate volatility and non-condensable gases escaping through the - 75°, - 100° and - 196°C traps. These were found to be CO_2, C_2-hydrocarbons and ketene, in agreement with earlier work on PVA (27,67) and vinyl acetate—ethylene copolymers (68). All the above volatile compounds and the non-condensable gases (CH_4, CO, H_2) are thought to result from the decomposition of the $CH_3COO\bullet$. Although some macromolecular scission may occur at this stage, it does not give gaseous products in this temperature interval.

The second stage in PVA degradation takes place between 375 and 500°C with a rate maximum around 430°C. In this stage, considerably less volatile material is produced, a large proportion of which is non-condensable at -196°C, and is formed by break up of the unsaturated polyene chain left after deacetylation.

At the end of the TVA experiment, the condensed fractions of different volatility were quantitatively determined by direct weighing giving the results presented in Table 4.1. The major fraction of products is the liquid fraction (63%), of which the major component is acetic acid, which is mostly formed in first stage of the degradation. The tar accounts for the 19% of the original polymer. The gas fraction accounts for 10.9%, of which the major proportion is decomposition products of acetate radicals.

Table 4.1 The material balance of the fractions collected during the degradation to 500°C of the poly(vinyl acetate) under TVA conditions.

No	Fraction	%
1	Condensable liquids of which	63
1a	Acetic acid	59.8
1b	Aliphatic hydrocarbons	0.3
1c	Aromatic hydrocarbons	2.8
1d	O-containing compounds	0.2
2	Cold ring fraction (tar)	19
3	Residue	8.1
4	Gases (non-condensable + C_2-C_4)	9.8
	Total	100.0

TABLE 4.2 TVA, DTG, TG and DSC data for PVA

TVA		DTG		TG	DSC	
Temp. range C	Peak temp.°C	Temp. range °C	Peak temp. °C	% weight loss for stage	Temp. range °C	Peak temp. °C
250-375	325	260-375	340	70	260-378	320
375-500	420	360-500	435	20	372-400	380

TVA, DTG, TG and DSC data are summarised in Table 4.2. A black carbonaceous residue (8—10%) was observed after the TVA experiment.

Subambient Thermal Volatilisation Analysis (SATVA)

Condensable volatile products from the TVA experiment were collected in a liquid nitrogen trap in the vacuum system, and were separated by SATVA. Mass spectroscopic analysis was carried out by bleeding the products evolved as the trap warmed gradually to 0°C into the mass spectrometer coupled to the TVA system. The condensable gases were also analysed by IR spectroscopy.

The SATVA trace (Fig. 4.4) shows five peaks. The initial small peak is due to some aliphatic hydrocarbons, mainly ethane. The second peak is due to CO_2, ketene and isobutene: this is confirmed by the IR spectrum of the peak 1 and 2 products (Fig. 4.5a) showing the presence of a large quantity of carbon dioxide through the absorption bands ν (2340, 3700 cm^{-1}) and δ (670 cm^{-1}), ketene may be identified from by its absorptions at 2150 and 2162 $cm.^{-1}$ However some of the isobutene is also distilled under the third peak, which is of very small magnitude. The material distilled at the fourth peak consisted mainly of light aromatic compounds, e.g. benzene, toluene, xylene. The IR spectra of peak 3 and 4 products (Fig. 4.5b) shows the presence of acetic acid through the (C=O) absorption at 1740 $cm,^{-1}$ unsaturation (C=C) at 1657 and 3057 $cm,^{-1}$ and isobutene through its characteristic band at 890 $cm.^{-1}$ The aromatic contents can also be seen through the absorptions at 1604 and 3084 $cm.^{-1}$ The fifth and largest peak is mainly due to acetic acid and other less volatile aromatic compounds of the liquid fraction.

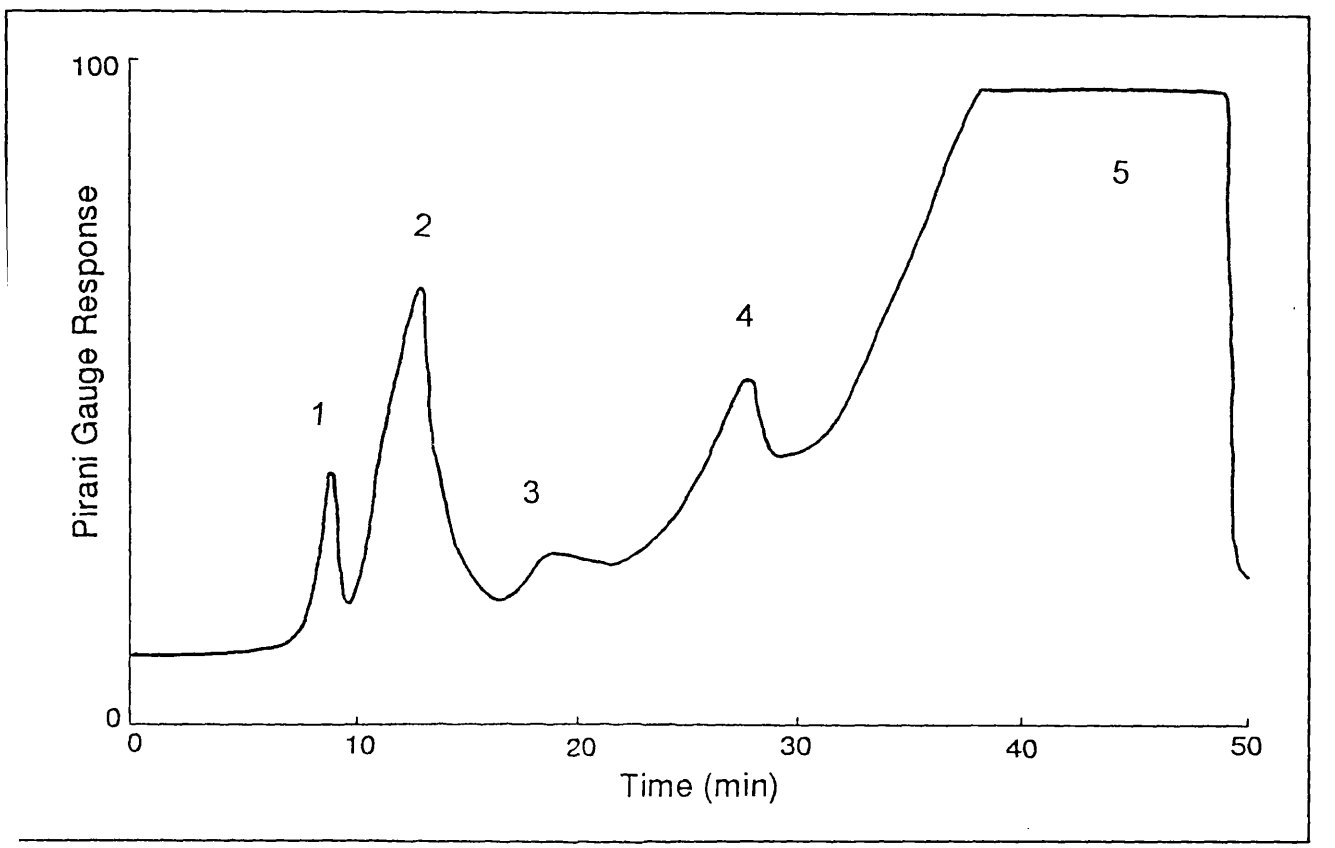


Fig. 4.4 SATVA curve of the degradation products, obtained under TVA conditions of PVA sample.

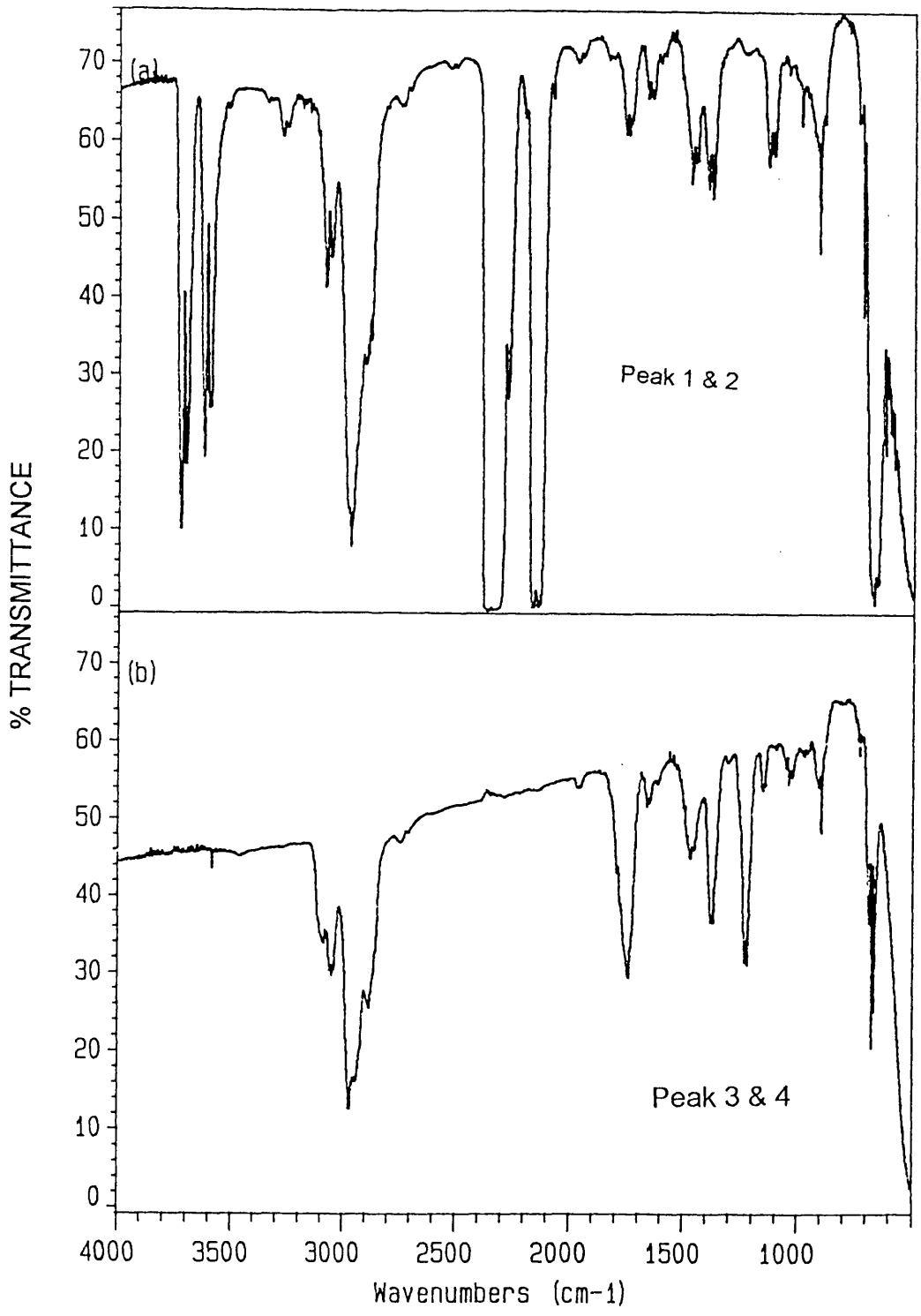


Fig. 4.5 Infrared spectra of the condensable gases and liquid fraction for degradation of PVA to 500°C under TVA conditions.

Table 4.3. Products of the thermal degradation of PVA to 500°C at 10°C/min, under vacuum established by the listed methods.

Noncondensable at -196°C	Condensable volatile Gases	Liquid Fraction	Cold ring fraction	Residue
MS only	IR & MS		IR MS & GC-MS	IR only
CO CH_4 hydrogen	CO_2 ethane propene ketene isobutene	acetic acid benzene toluene, xylene ethylbenzene styrene	acetate groups aromatic contents e.g. di- and tri- substituted benzene rings aromatic ketones	black carbonaceous residue with heavily condensed aromatic rings

Table 4.4 The composition of the liquid fraction collected during the pyrolysis of PVA after the removal of acetic acid

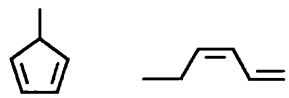
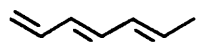
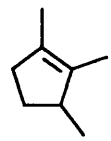
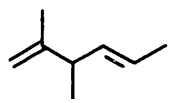
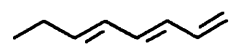
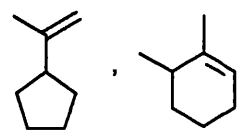
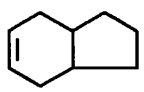
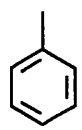
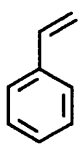
	Compound	MW	%
	Aliphatic Hydrocarbons		
1		80	1·0
2		94	1.2
3		110	1·0
4		—	0·9
5		100	0·9
6		110	0·5
7		122	0·5
	Others[a]	—	2·7
	Total Aliphatic	—	8·7
	Aromatic Hydrocarbons		
8		78	2·8
9		92	29·0
10		104	6·8

Table 4.4 (continued)

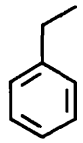
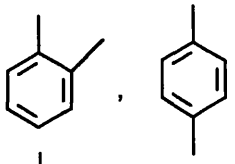
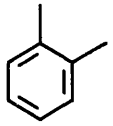
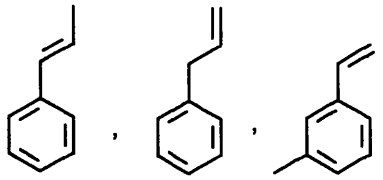
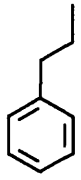
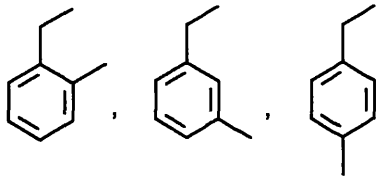
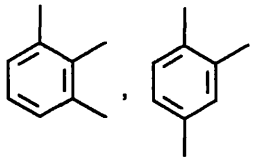
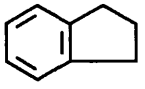
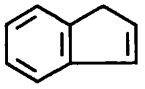
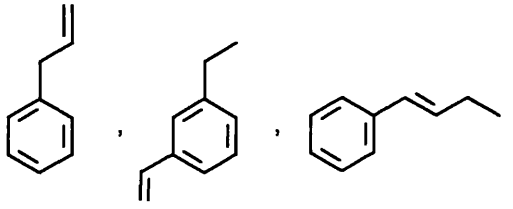
Compound	MW	%
11 	106	9·4
12 	106	5·4
13 	104	8·5
14 	118	2·0
15 	120	2·3
16 	120	3·5
17 	120	0·5
18 	118	1·6
19 	116	0·7
20 	132	0·5

Table 4.4 (continued)

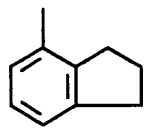
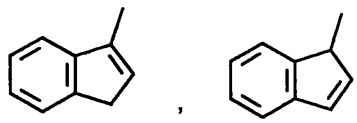
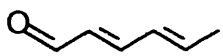
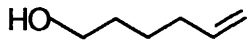
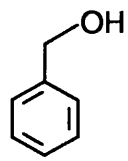
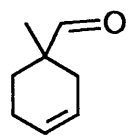
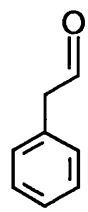
	Compound	MW	%
21		132	0·5
22		130	0·5
	Others [a]	—	11·3
	Total aromatic hydrocabons	—	85·3
	Oxygen-containing compounds		
23		96	1·5
24		100	0·5
25		112	1·7
26		124	1·2
27		134	0·5
	Others [a]	—	0·6
	Total	—	6·0
	Total General		100·0
	Under 0.5% each		

Table 4.3 summarises the products in the various degradation fractions. In the case of liquid fraction only the volatile products which were identified by IR spectroscopy and on-line mass spectroscopy are listed.

The liquid fraction collected during the TVA experiment has also been examined by the GC-MS technique after removing acetic acid.

The major product of the liquid fraction is acetic acid. The products of liquid fraction analysed by GC-MS are listed in Table 4.4. The important products are toluene, xylene isomers and benzene.

COLD RING FRACTION (CRF)

The mass of CRF, the volatile material that condensed in the upper part of the TVA tube, was determined by weighing. A suitable solvent was used to transfer the material to a weighing bottle after which the solvent was removed by evaporation.

The infrared spectra of undegraded and degraded polymer are compared in Fig. 4.6 (a & b) and the main peaks are listed in Table 4.5. The IR spectrum of the tar shows relatively high aliphatic content (2960-2860, 1460, 1380 cm^{-1}) bearing some acetate groups (1734, 1240, 1170 cm^{-1}). The tar also has significant aromatic content, seen through absorptions at (3070, 3020, 1620 cm^{-1}), with a variable degree of substitution (890, 810, 750, 700 cm^{-1}), although di- or trisubstituted aromatics (750 cm^{-1}) are predominate.

Mass spectrometry, using a probe heated to 150 and 250°C (Fig. 4.7a-b) shows a mixture of the materials with molecular size up to approximately 350 and 600 respectively. The CRF was also examined by GC-MS technique.

Table 4.5. Assignment of the major peaks in the IR spectrum of undegraded PVA.

Band (cm^{-1})	**Assignment**
2980	CH_3 asymmetric (C—H) stretch
2930	CH_2 asymmetric (C—H) stretch
2870	CH_3 symmetric (C—H) stretch
1745	C=O stretch of ester group
1460	CH_2 bending deformation
1435	CH_3 asymmetric bending
1375	CH_3 symmetric bending
1248	(C—O—C) symmetric stretching
1130	(C—O—C) symmetric stretching
1025	(CH—O) symmetric stretching
950	(C—CH_3) rocking
800, 605	(O—CO) Bending and other deformations (74)

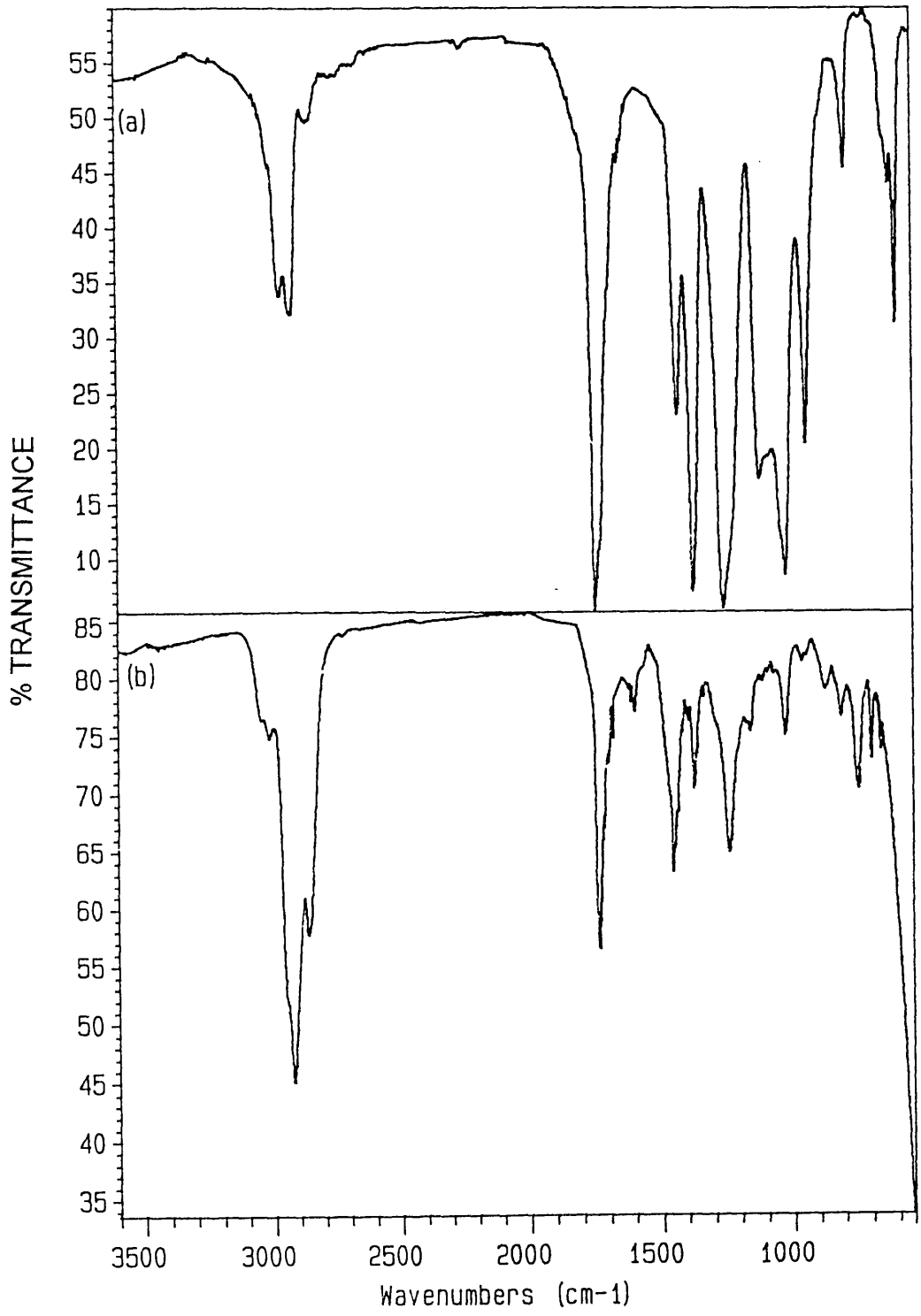


Fig. 4.6 IR spectra of (a) undegraded copolymer (b) cold ring fraction of PVA degraded to 500°C under TVA conditions.

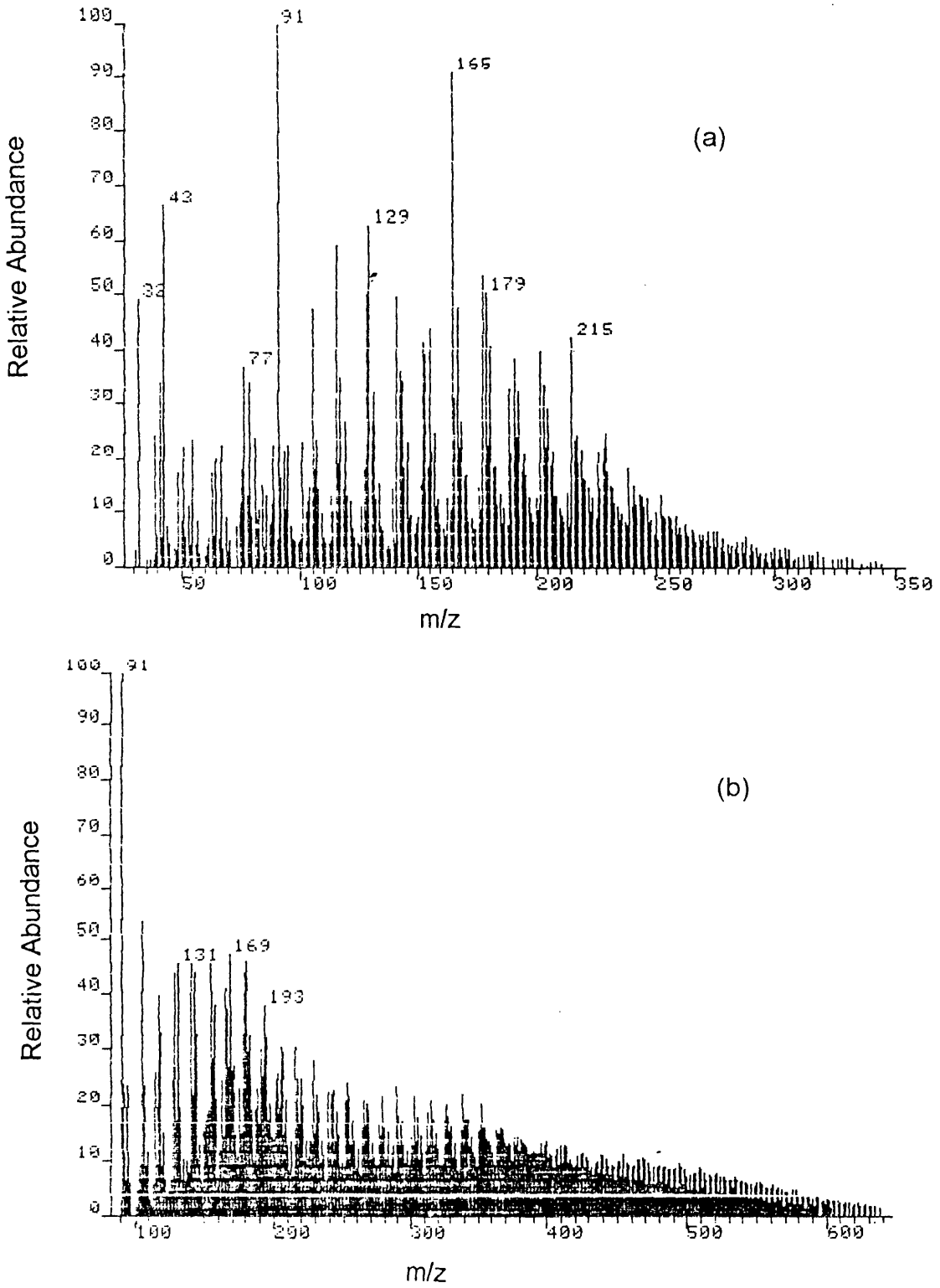


Fig. 4.7 Mass spectra of cold ring fraction (CRF) from the degradation of PVA to 500°C under TVA conditions using probe temperatures of (a) 150°C (b) 250°C.

Table 4.6 The composition of the cold ring fraction collected during the pyrolysis of PVA. (The products are listed according to their relative abundance)

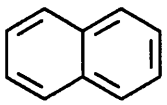
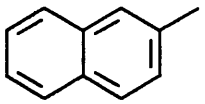
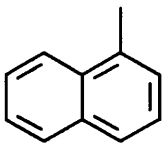
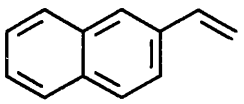
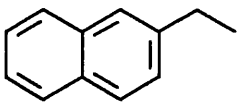
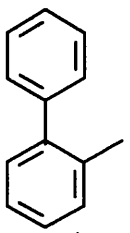
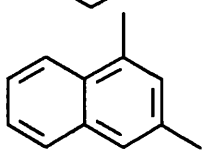
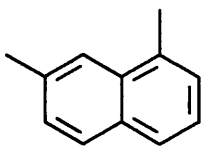
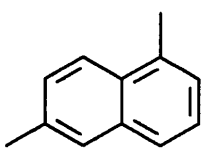
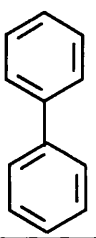
	Compound	MW
1		128
2		142
3		142
4		154
5		156
6		168
7		156
8		156
9		156
10		154

Table 4.6 (continued)

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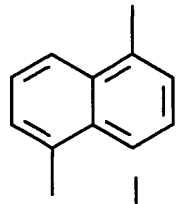
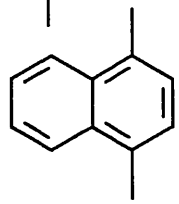
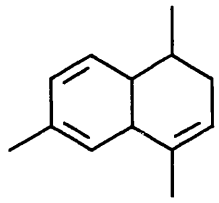
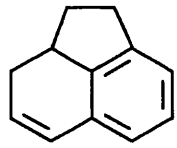
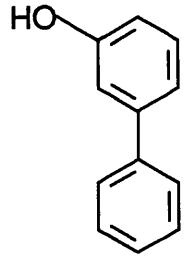
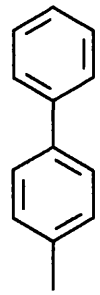
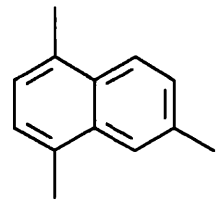
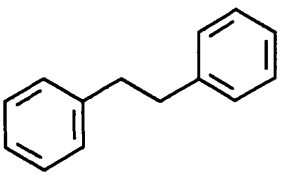
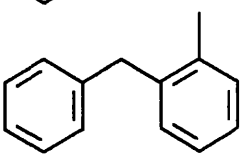
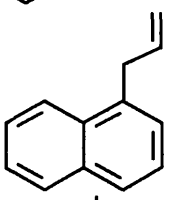
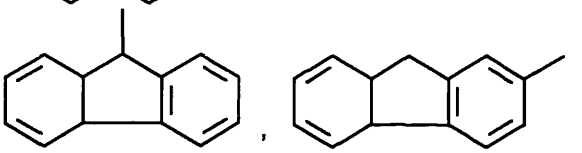
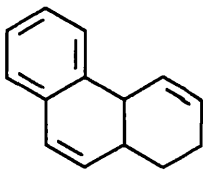
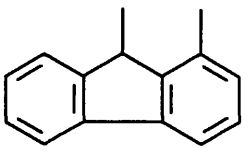
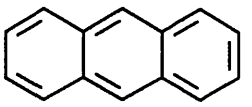
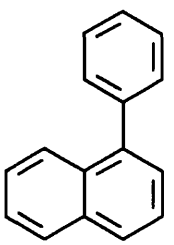
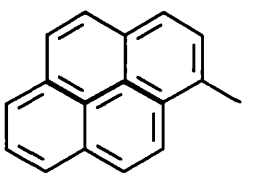
11		156
12		156
13		172
14		154
15		170
16		168
17		170

Table 4.6 continued

	Compound	MW
18		182
19		182
20		168
21		180
22		182
23		194
24		178
25		204
26		216

The products identified of CRF are listed in Table 4.6 according to their relative abundance.

The tar consists of large breakdown fragments of what has become a polymeric network after 380°C. The spectrum of the tar resembles the spectrum of PVA heated up to 380-400°C (Fig. 4.8d-e), hence it is apparent that the tar components break down at the beginning of second stage (around 350°C).

The breaking points could be the tertiary C atoms in the C_6 ring (66) that has been formed through Diels-Alder condensation, if the ring has failed to become aromatic.

FTIR-SPECTROSCOPIC INVESTIGATION OF STRUCTURAL CHANGES DURING THE DEGRADATION OF POLY(VINYL ACETATE)

The structural changes in the vinyl acetate polymer during thermal degradation have been investigated by FTIR reflection absorption spectroscopy using a film cast on stainless steel high reflection plate.

A film of polymer sample was cast on the plate as follows. Firstly a saturated solution of 5 mg of polymer sample in acetone was poured and uniformly spread onto the plate. The acetone was allowed to evaporate at room temperature. The apparently dried film was then kept in a vacuum oven at 40°C for 48 hrs and finally heated at 100°C for 20 minutes to evaporate any remaining solvent.

Typically, in a temperature programmed experiment the changes in polymer structure were followed by heating the polymer film at a rate of 10°C/min to

different temperatures up to the point of char. The heated film was then cooled rapidly with fan assistance at a rate of approximately 50°C/min. FTIR spectra were taken using reflection-absorption apparatus. In some cases a diffuse reflectance spectrum was obtained, in which case the spectra were subjected to automatic deconvolution.

The structural changes upon heating at temperature from 160 to 480°C are illustrated in Fig. 4.8 (b-f). The main absorption bands of undegraded polymer (Fig. 4.8a) are summarised in Table 4.5. The spectrum shows small shoulders at 3020 and 1657 cm^{-1} due to a low concentration of double bonds already present in the reference material.

The elimination of acetic acid and the formation of unsaturation can be clearly seen in the spectrum of PVA heated up to 200°C (Fig. 4.8b).

At 360°C, the absorption bands at 3020 and 1657 $cm,^{-1}$ characteristic of the internal unsaturation, are developed (Fig. 4.8c). At the same time, there are signs of aromatisation: new bands at 1560, 1520, 760 cm^{-1} and the 1435 cm^{-1} band moves to 1455 $cm.^{-1}$ Other transformations in the spectrum are related to the decay of ester groups (various bands in the region 1248-600 cm^{-1}) and the CH_3 group associated with it (the 2980 cm^{-1} band disappears completely and the intensity of the 1375 cm^{-1} band is reduced). Another feature of the spectrum is that the absorption at 2870 cm^{-1} has increased, which is a feature of polynuclear aromatic systems. Solubility tests carried throughout the degradation experiment showed that PVA is soluble in acetonitrile after degradation up to 300°C, but becomes insoluble if heated to higher temperatures.

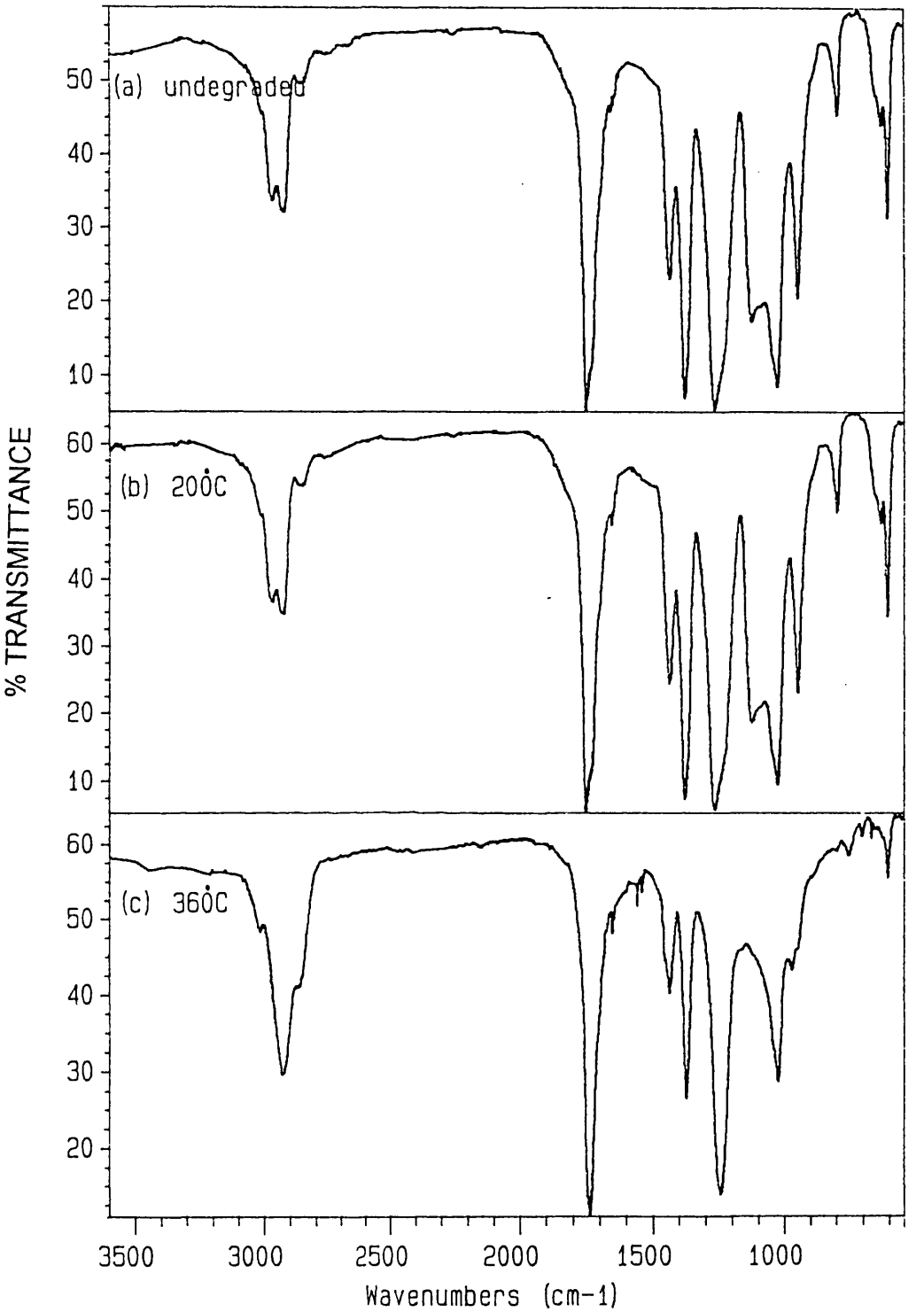


Fig. 4.8 Infrared spectra of PVA: (a) before and after heating in vacuum to: (b) 200°C (c) 360°C.

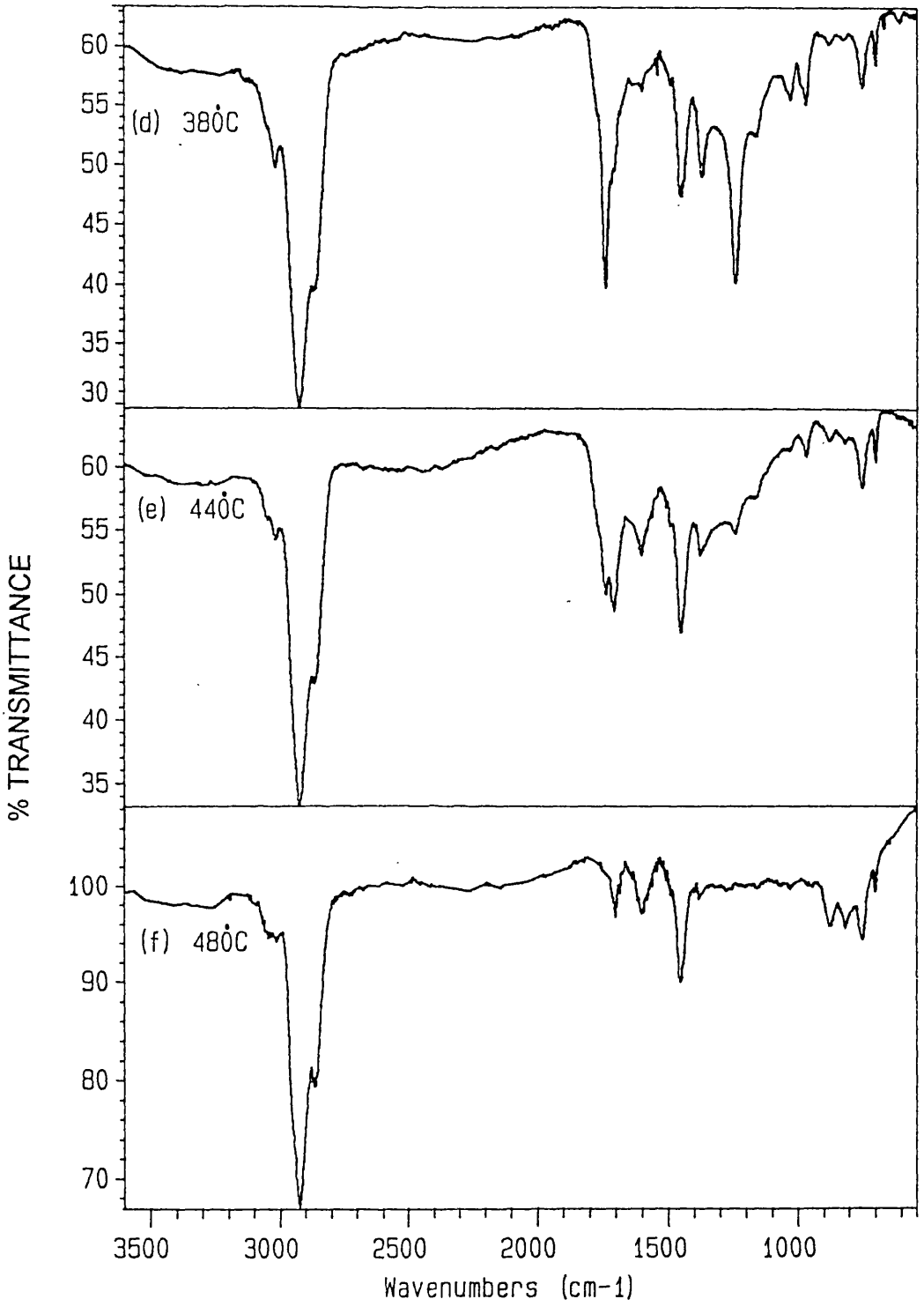


Fig. 4.8 Continued (d) 380°C (e) 440°C (f) 480°C.

In PVA heated up to 380°C (Fig. 4.8d) the aromatisation is extended as shown by increased absorptions at 3020, 1600, 1560, 1450 cm^{-1} and the presence of the bands at 760 and 700 cm^{-1} due to the aromatic C—H out of plane bending. The band at 1657 cm^{-1} and the shoulder at 3060 cm^{-1} show the appearance of end type unsaturation formed on the hydrocarbon chain through scission, however, the 3060 cm^{-1} band could be also due to the presence of aromatic structures. A few ester groups still survive as can be seen through absorption bands 1734, 1240 and 1170 $cm.^{-1}$ A new absorption band appears at 1706 cm^{-1} (C=O) with its overtone above 3200 cm^{-1} and a shoulder band at 1160 $cm.^{-1}$ This suggest that an aliphatic ketone in the vicinity of unsaturation is formed. The possibility of the presence of retained acetic acid has been ruled out as continuous evacuation of the very thin film prevents its accumulation.

The spectrum of the polymer heated up to 440°C (Fig. 4.8e) shows that few ester groups have survived and it also shows the extended features of aromatisation in the system. The structure of the polymer heated up to 480°C (Fig. 4.8f), shows similar features to the char. There is a high content of aromatic rings showing the out of plane bending of one (870 cm^{-1}); two (820 cm^{-1}); three and four (760 cm^{-1}); and five H atoms (700 cm^{-1}). These aromatic rings are predominantly di- or trisubstituted, but most probably condensed. A number of them are monosubstituted. It is difficult to establish the content or the structure of the aliphatic residue as its bands overlap with those of the polycyclic aromatic system in the CH stretching region. Ketone groups are situated on the hydrocarbon chain, probably α, β– unsaturated, as shown by the fact that the ν C=O vibration is situated at 1760 cm^{-1} and the ν C=C vibration initially present at 1657 cm^{-1} is now displaced to lower wave numbers, overlapping the aromatic ν C=C absorption at 1600 $cm.^{-1}$

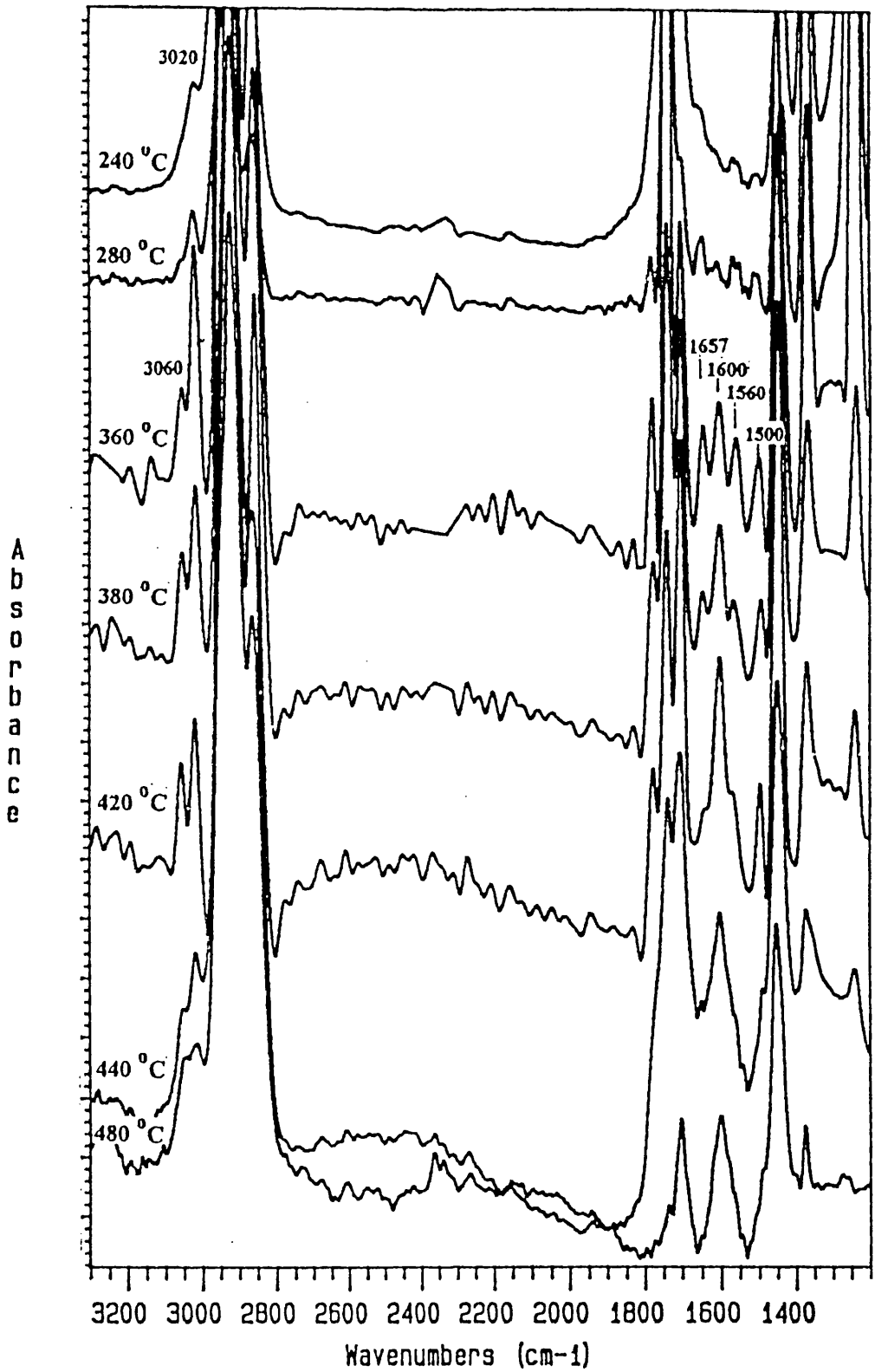


Fig. 4.9 FT-IR spectra of thermally degraded PVA obtained by deconvolution.

Through Fourier self-deconvolution the peaks in the regions 3100-3000 cm^{-1} and 1670-1500 cm^{-1} were better resolved and the building up of aromatisation resulting from the development of unsaturation with increase of temperature can be followed (Fig 4.9).

DISCUSSION

In the light of the above experiments it is clear that poly (vinyl acetate) (PVA) decomposes in two well defined stages. TVA and TG results shows that in the first stage (250-375°C), a massive amount of acetic acid is produced, progressively forming polyene chain. In the second stage (375-500°C), the conjugated polyene chain formed in the result of deacetylation is severely fragmented, leaving some char residue.

From the analysis of the IR spectra it is clear that, in PVA, unsaturation begins to appear in the chain at 160°C. The nature of unsaturation is known from the literature: mainly isolated double bond and diene, but also some longer polyenes (66).

After deacetylation, aromatisation is the next important process that occurs in the first stage of degradation. It is evidenced from IR studies that aromatisation begins around at 280°C, moreover at 350°C, the polymer become insoluble. The aromatic rings are di- and trisubstituted and seem to be condensed even when they first appear. A number of rings, however, are monosubstituted. Some ester groups survive to 440°C, but they are soon transformed into ketone (α, β -unsaturated) formed on a the aliphatic chain.

Material balance of PVA after degradation by TVA presented in (Table 4.1), shows that PVA, produces a liquid fraction about 63%. Acetic acid accounts for 95% of its composition and for 59.8% of the PVA. Being the only liquid

product in the first stage of degradation, it could be collected and weighed. The liquid fraction collected in the second stage from 370-500°C contains only 0.65% acetic acid as determined by GC-MS (without Na_2CO_3 pretreatment).

The other liquid compounds formed in the PVA pyrolysis are also presented in Table 4.1. Among them, aromatic hydrocarbons prevail, accounting for 2.8% of the polymer weight. PVA also gives a moderate fraction of tar (19%) and a small fraction of gases (9.8%).

On the basis of the GC-MS quantitative evaluation of the O- containing products in the liquid fraction, it was calculated that 1% of the acetate groups initially present in the polymer from these products. The FTIR spectrum of the tar (Fig. 4.6b) shows that acetate groups are also present in the tar. From the amount of the acetic acid formed (59.8%) and theoretical content in acetate groups of PVA one can calculate that about 8.8% acetate groups are eliminated with the tar. Hence, 9.8% of the acetate groups fail to deacetylate producing acetic acid and unsaturation.

9.8% of acetyllate groups fail to decompose, i.e. roughly one in ten. This suggests statistically that the average spacing of the remaining side groups would be ten units, corresponding to an unsaturated conjugation length of five. This would confirm findings by Gardner and McNeill (27) who stated that the predominant unsaturated product length was six.

Table 4.1 shows that PVA gives a moderate fraction of tar (19%) and a small fraction of gases (9.8%). However, the picture changes if we consider that after 360°C we are dealing in practice with a modified polymer accounting for 40% of initial weight of the PVA. Consequently, the amount of tar (19%) appears important (practically half of the polymer which remains after deacetylation). The other half suffers intense reorganisation to condensed

rings which are retained in the char (8%) as well as massive fragmentation which releases an important fraction of gases (9.8%) and a very small fraction of liquids (3.3%).

The composition of the liquid fraction (after removal of acetic acid) is presented in Table 4.4. The main components are the aromatic hydrocarbons, which constitute 85% of the liquid fraction and 2.8% of the whole polymer. The main component of the liquid fraction is toluene which accounts for 29% of the fraction and for 1% of the PVA. It is followed by ethyl benzene, xylene isomers and styrene.

Unlike PVC which produces mainly benzene as a result of double bonds formed through dehydrochlorination, PVA forms toluene with a higher probability.

The major product of PVA degradation, acetic acid, is formed in two reactions (25,58,69,27) : an apparently random elimination of acetate groups forming isolated double bonds and a zip deacetylation process forming conjugated polyene sequences in the polymer backbone which on the basis of UV spectroscopic evidence can have a length of up to six double bonds (27). However, the average length of unsaturated sequences in PVA in the early stages of degradation is low (1.5 double bonds at a degree of deacetylation of 0.6%) (70) showing that the elimination of a single acetic acid molecule at some sites is the starting process.

Some of acetic acid from PVA degradation may be produced by purely molecular elimination but there is evidence to support the view that a radical mechanism is important. This allows the effect of PVA in causing some depolymerisation of PMAA in PVA—PMAA blends at abnormally low temperature (60) and the formation of ketene and carbon dioxide from PVA at temperatures below those required to decompose acetic acid to be

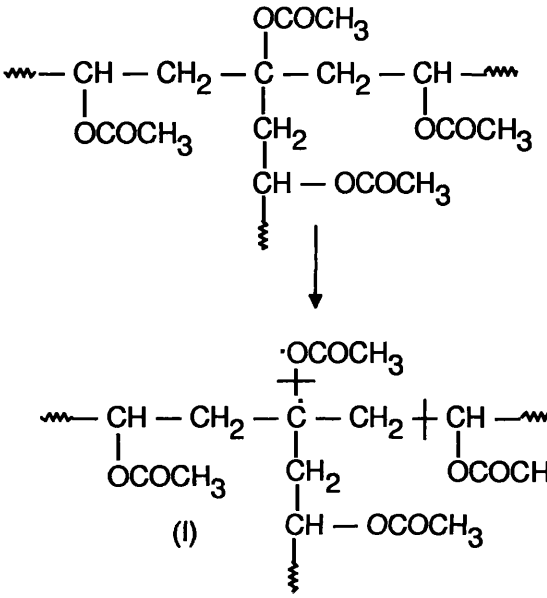
explained. The presence of some minor O- containing products found in the present investigation also requires O- containing free radical intermediates. A homolytic route for zip deacetylation has been proposed by McNeill (6) and is included in the more detailed mechanistic scheme for PVA degradation presented here.

The site at which the first side group homolysis takes place to give a $CH_3COO\cdot$ radical has not been clearly identified. It has been suggested that labile site for the initiation of PVA thermal degradation is the acetate group attached to the quaternary carbon atoms at a branching point, (70) although definite proofs are still lacking. The above hypotheses is derived by analogy with PVC. The most numerous branches are long, nonhydrolysable ones formed through the chain transfer of a growing radical to the methine carbon bearing the acetate group (71). A similar structure also appears at the branching points C_4 branches formed through 1,5 backbiting and C_2 branches 'clustered' as a result of several backbiting acts following the addition of one monomer unit (72).

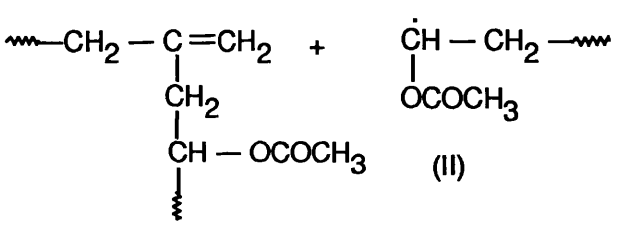
It is considered in the (reaction 1 Scheme 1) that the initiation by the thermal dissociation of the acetate groups is at branching points. This leads to a macroradical I which provides the source for the process leading to the observed products. Radical I would be expected to split creating radical II and a macromolecule with chain end unsaturation (reaction 2). Radical II is the growing radical in PVA polymerisation and it is not expected to give zip deacetylation. Since it is not stabilised by resonance, it has a high reactivity in H abstraction its site of attack being the methane H, by abstraction of which radical III is formed (71,72). Radical III suffers scission as in reaction 3 and cannot explain the zip deacetylation. Reaction 1-3 could explain why PVA forms a great number of isolated double bonds in the early stages of degradation (70).

Mechanisim for degradation of poly (vinyl acetate)

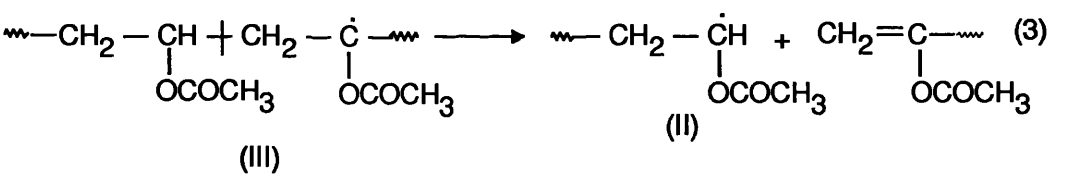
Scheme 1



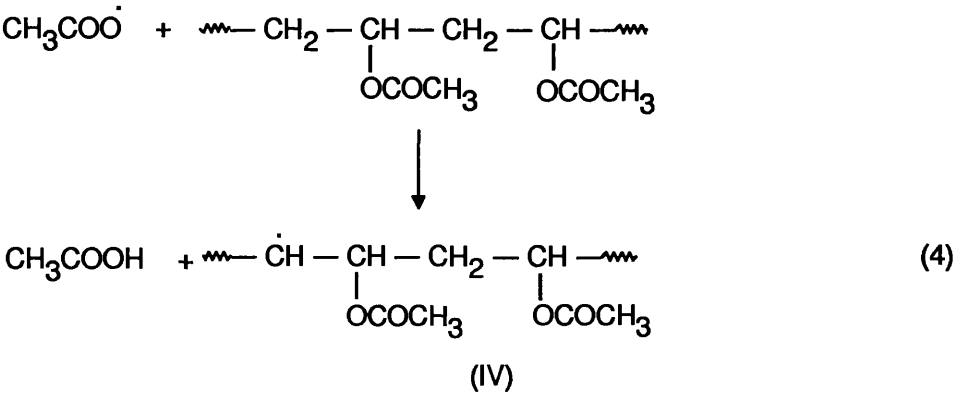
(1)



(2)

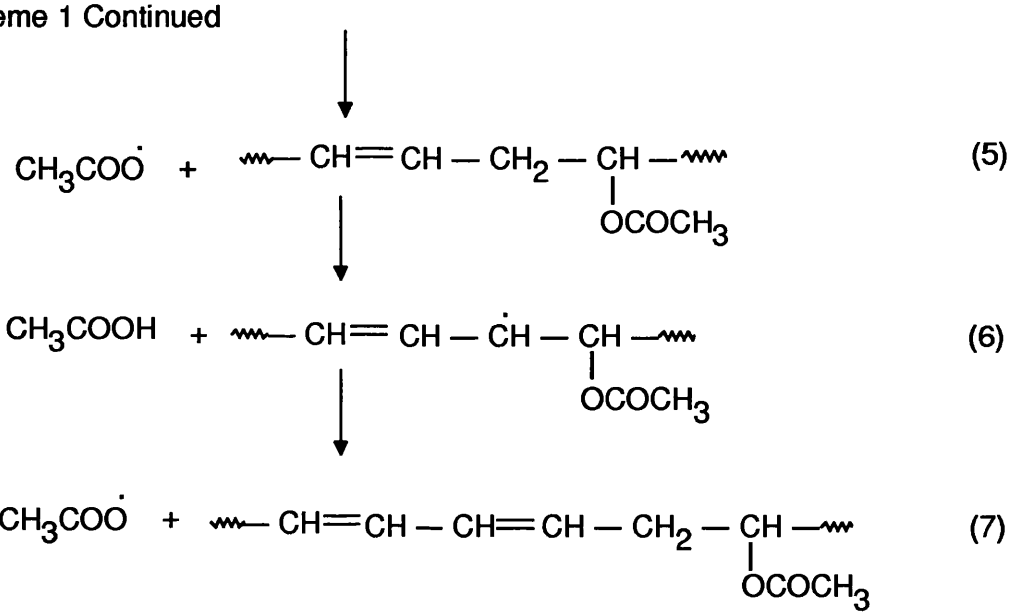


(3)



(4)

Scheme 1 Continued

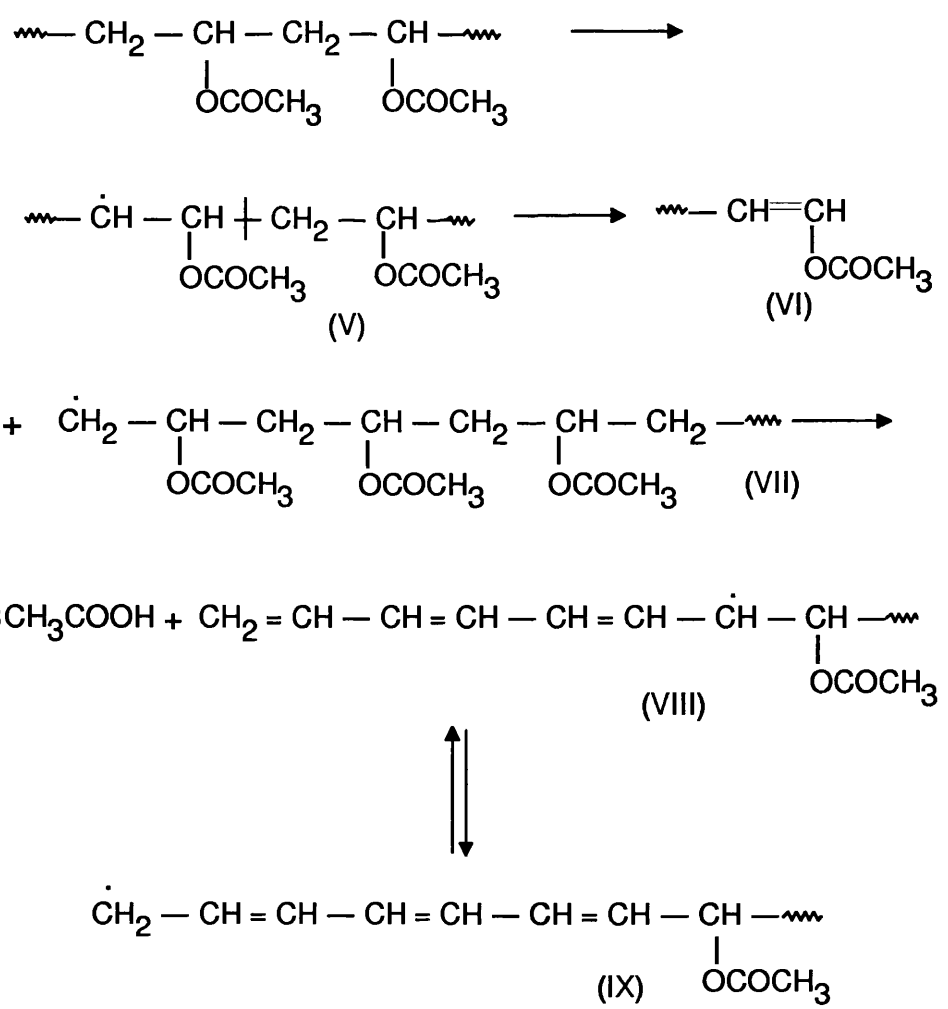


(5)

(6)

(7)

Scheme 2



(V)

(VI)

(VII)

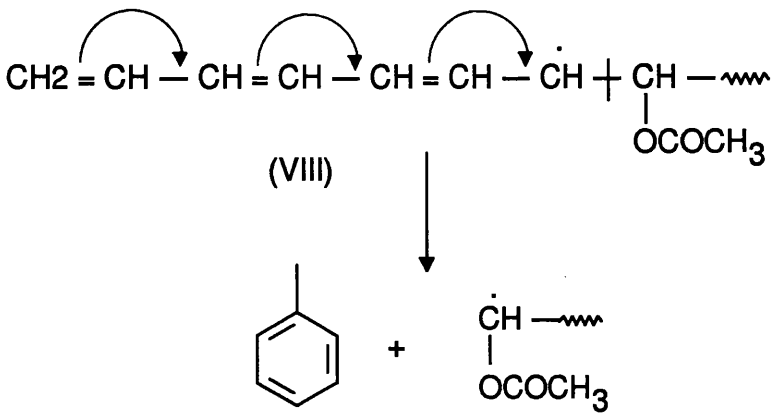
(8)

(VIII)

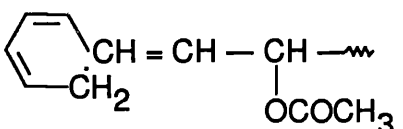
(9)

(IX)

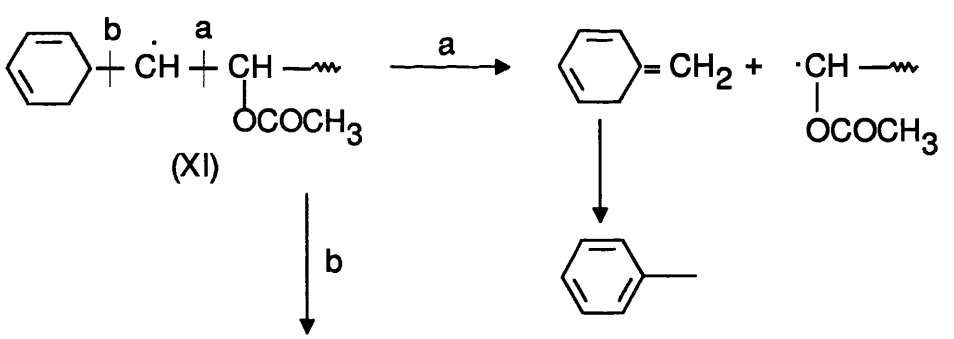
Scheme 2 Continued



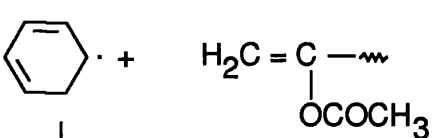
(10)

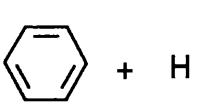


(X)



(11)





(12)

Reaction 1 forms an important number of acetoxy radicals as the number of branches in commercial PVA is quite high (10-20/100 VA units 70). The deacetylation as a chain reaction propagated by acetate radicals is described

by equations (4)-(7). Oxygen centred radicals are known to be much more reactive in H abstraction and less specific regarding the site of attack than carbon centred radicals (73).

Scheme 2 tries to explain the formation of toluene in which a free radical (V) appears as a result of H abstraction which breaks the chain to give radical (VII) which through deacetylation can easily give radical (VIII) (reaction 8). Radical (VIII) is isomeric with radical (IX) (reaction 9). Radical (VIII) is more stable being a secondary radical. Radical (VIII) cannot split the bond with the unsaturated C_6 chain at the left because of the increased bond strength through conjugation. The adjacent bond to the right with a tertiary C atom bearing acetate group (quite neutral) is slightly polarised towards the neighbouring conjugation and is strained. This can be broken easily generating toluene (reaction 10). Alternatively, aromatic hydrocarbon formation can be explained by reactions (11-12) involving radical (X). This radical attacks the double bond at the sixth carbon atom, closing a cycle forming radical (XI). Radical (XI) seems to have an equal probability of splitting either of the adjacent bonds forming benzene and toluene. The fact that (X) is more stable than (XI) can explain the higher probability of toluene formation.

CONCLUSION

PVA presents two degradation stages. In the first stage, between 200-360°C it eliminates 90% of its acetate groups as acetic acid accumulating double bonds. Around 280°C, the double bonds belonging to different chains begin

to condense through a Diels-Alder reaction giving aromatic rings embedded in an aliphatic network which bears 10% of the initial acetate groups. In a second stage of degradation, between 360-480°C there are reorganisations consisting in the massive scission of the aliphatic network at the tertiary and the quaternary C atoms of the non-aromatic cycles followed by the elimination of large fragments of low volatility which form the tar.

After the acetic acid fraction (accounting for 60% of the initial polymer) the tar is the second most important fraction (19%). The tar is largely aliphatic, containing 9% of the acetate groups initially present in PVA and few aromatic rings. 1% of the acetate groups survive in the charred polymer after the tar elimination and form, in the second part of stage II, the oxygen-containing products in the liquid fraction, which are aliphatic and aromatic aldehydes and alcohols. The liquid fraction remaining after the removal of acetic acid is low (3%) and so is the gas fraction (9.8%). The polymer leaves 8% char at 500°C

containing mainly condensed aromatic rings and, to a small extent, an aliphatic chain with α,β–unsaturated ketone groups.

The analysis of the liquid fraction shows that aromatic hydrocarbons are the main components with toluene being the major product (29%). Unlike PVC which forms benzene upon dehydrochlorination, PVA forms toluene upon deacetylation. The preferential formation of toluene has been explained in terms of increased probability for bond scission in the radical intermediate leading to toluene. During degradation, PVA has a strong tendency to crosslink, due to, the presence of double bonds formed through acetic acid elimination.

CHAPTER FIVE

THERMAL DEGRADATION OF POLY (METHACRYLIC ACID)

INTRODUCTION

The thermal decomposition of poly(methacrylic acid) (PMAA) has been the subject of many studies (75-78,28). Bresler, Keton and their co-workers reported that poly(methacrylic acid) PMAA produces cyclic structures when water is liberated and is also more thermally stable than its parent substance methacrylic acid (75). In later studies it was established that PMAA decomposes in two stages involving an initial dehydration at around 200°C to give a cyclic anhydride and at higher temperatures the polyanhydride decompose to give various fragments, including some volatile products i. e. CO_2, CO and traces of alkene and leaving a small amount of carbonaceous residue (76-78).

Grant and Grassie (28) found that depolymerisation also occurs to a small extent also resulting in a small yield of monomer. This reaction, however, is effectively prevented by the predominating dehydration reaction. The residual product predominantly consists of linked six-membered anhydride rings with occasional crosslinks.

In the present studies the thermal degradation behaviour of poly(methacrylic acid) has been studied in detail and a mechanism of decomposition has been proposed. The polymer was prepared by bulk polymerisation at ambient temperature using AIBN as initiator. The polymerisation method is described in chapter Three while the preparation conditions are given in Table 5.1.

Table 5.1 Preparation conditions for the poly(methacrylic acid) by bulk polymerisation.

Amount of methacrylic acid	21 g
Amount of initiator (AIBN)	0.05 %*
Time of polymerisation	4 hours
Temperature of polymerisation	Ambient temperature
Conversion	3.5 %

* Relative to the total weight of monomers

THERMAL DEGRADATION

Thermal degradation of poly(methacrylic acid) has been studied by using TVA, TG, DTG and DSC techniques under different environment e.g. nitrogen conditions and under vacuum conditions. Degradation products obtained under TVA conditions were also examined. The various degradation fractions (cold ring, liquid fraction, residue) were weighed for material balance after pyrolysis. The gases were determined by difference.

The structural changes in the polymer during the degradation have been investigated, typically in programmed heating experiments at 10°C/min to a chosen ceiling temperature.

THERMOGRAVIMETRY (TG)

The thermogravimetric (TG) and differential thermogravimetric (DTG) curve for PMAA were obtained under dynamic nitrogen at a heating rate of 10°C/min. The curve shows two stages of polymer breakdown. The first, between 200 and 280°C, involves 18% weight loss, which is mainly due to formation of water through dehydration. The theoretical maximum weight loss of water from anhydride formation is 10.47% of the original sample weight, which is less than the 18% weight loss recorded. Since the TVA trace shows that a small fraction of CO_2 is also formed in this temperature region, then a fraction of the COOH groups must suffer decarboxylation, while of a very small amount of methacrylic acid is formed through depolymerisation, explaining the difference between the theoretical and observed weight loss.

Over the temperature interval 280-330°C, the residual polymer is stable, protected by the anhydride groups. PMAA suffers extensive degradation between 350 and 475°C, and a considerable weight loss of 70% is observed in this temperature interval. At this stage anhydride rings decompose with the elimination of CO and CO_2 accompanied by backbone scission.

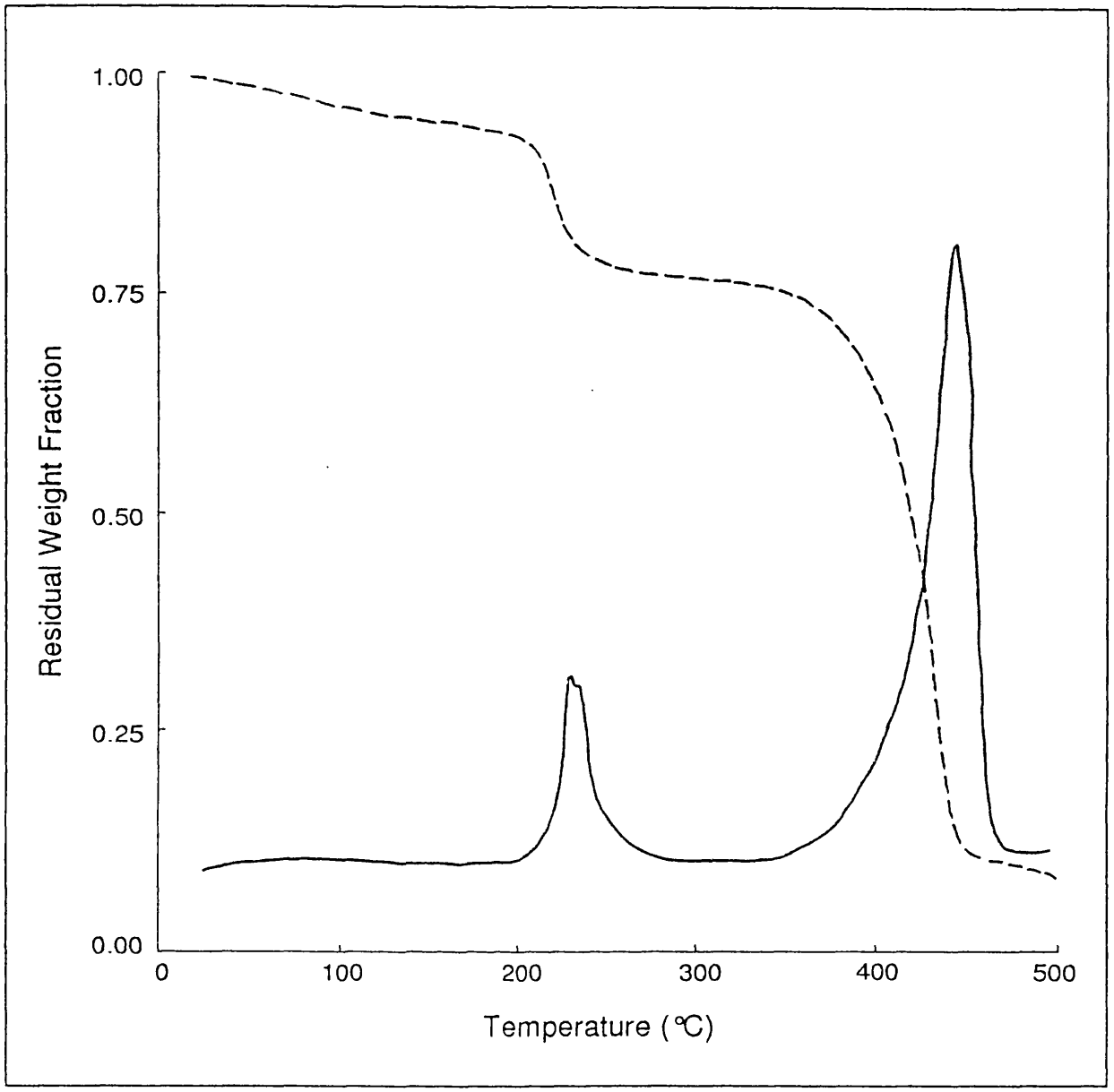


Fig. 5.1 TG and DTG curve obtained (heating rate 10°C/min, nitrogen flow) for PMAA sample.

The maximum decomposition rate of the anhydride is at 440°C, as shown by the asymmetrically-placed inflection point on the DTG curve, close to 420°C, the temperature at which aromatic rings appear quite suddenly in the FTIR spectrum (66). PMAA leaves 4% residue of the original sample weight at 500°C, indicated by TG.

DIFFERENTIAL SCANNING CALORIMETRY

PMAA degradation was also studied by differential scanning calorimetry (DSC). A sample in powder form of approximately 5 mg was heated up to 500°C at 10°C/min under nitrogen flow of 70ml/min. The result obtained for the polymer is presented in Fig. 5.2, with the features are listed in Table 5.2.

The curve shows a large endotherm in the temperature region 200 to 280°C with a thermal effect of (441J/g). This endotherm corresponds to a weight loss of 18% observed in the first stage of decomposition on the TG curve. It is interesting to note that there is a splitting of the peaks in the DSC and TG traces in the temperature region 200-280°C, suggesting that two reactions are taking place. This feature will be discussed later.

The DSC curve shows another endotherm in the temperature region 400 to 475°C with an enthalpy change of 215J/g. This endotherm corresponds to the weight loss indicated by TG at higher temperature.

THERMAL VOLATILISATION ANALYSIS

The TVA experiment was conducted up to 500°C at a heating rate of 10°C/min, under continuous evacuation, with 60 mg of polymer spread as a thin layer in a silica boat. The TVA system, illustrated in Chapter Two, contained five Pirani gauges situated after traps cooled to 0°C, -45°C, -75°C, -100°C and -196°C respectively.

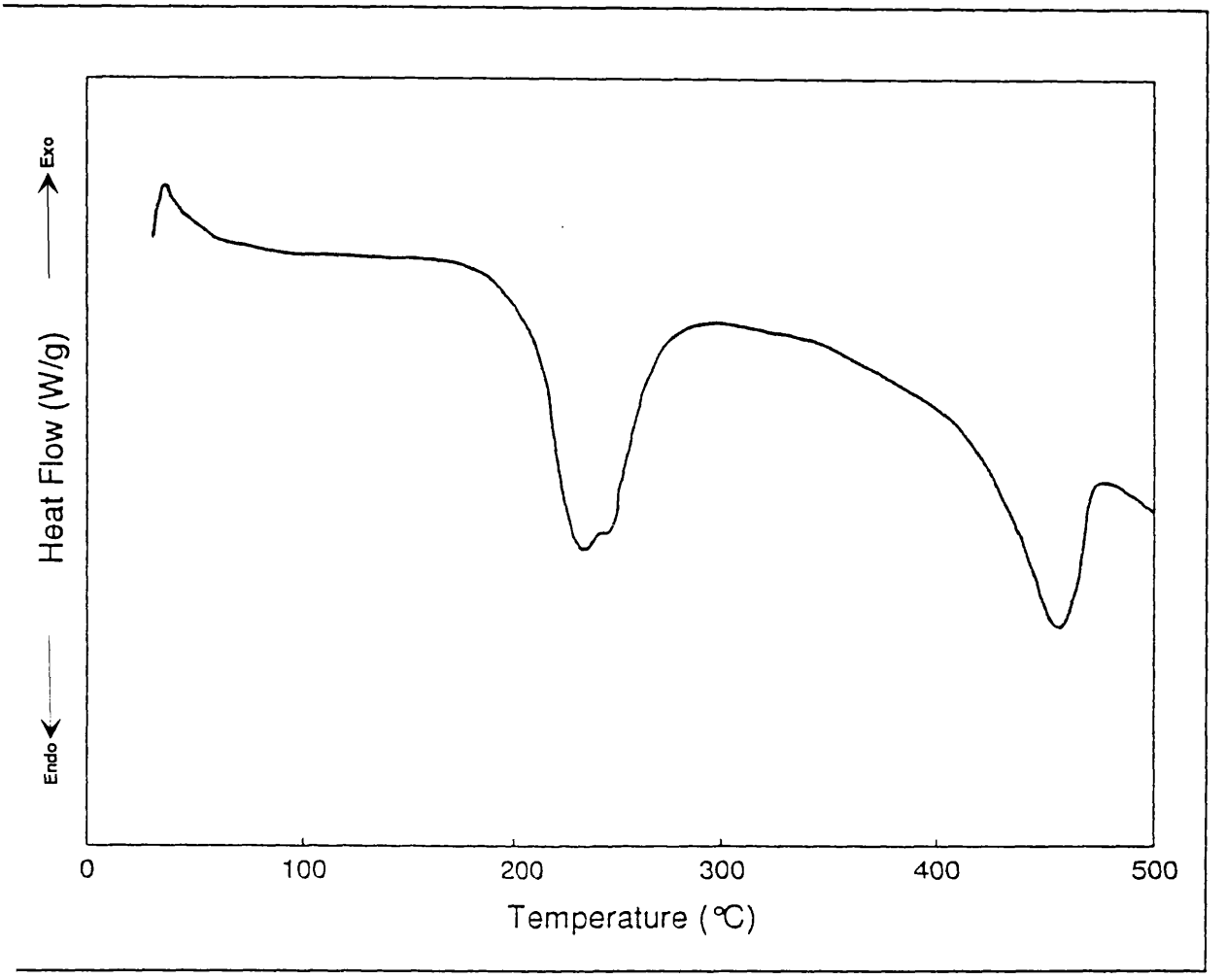
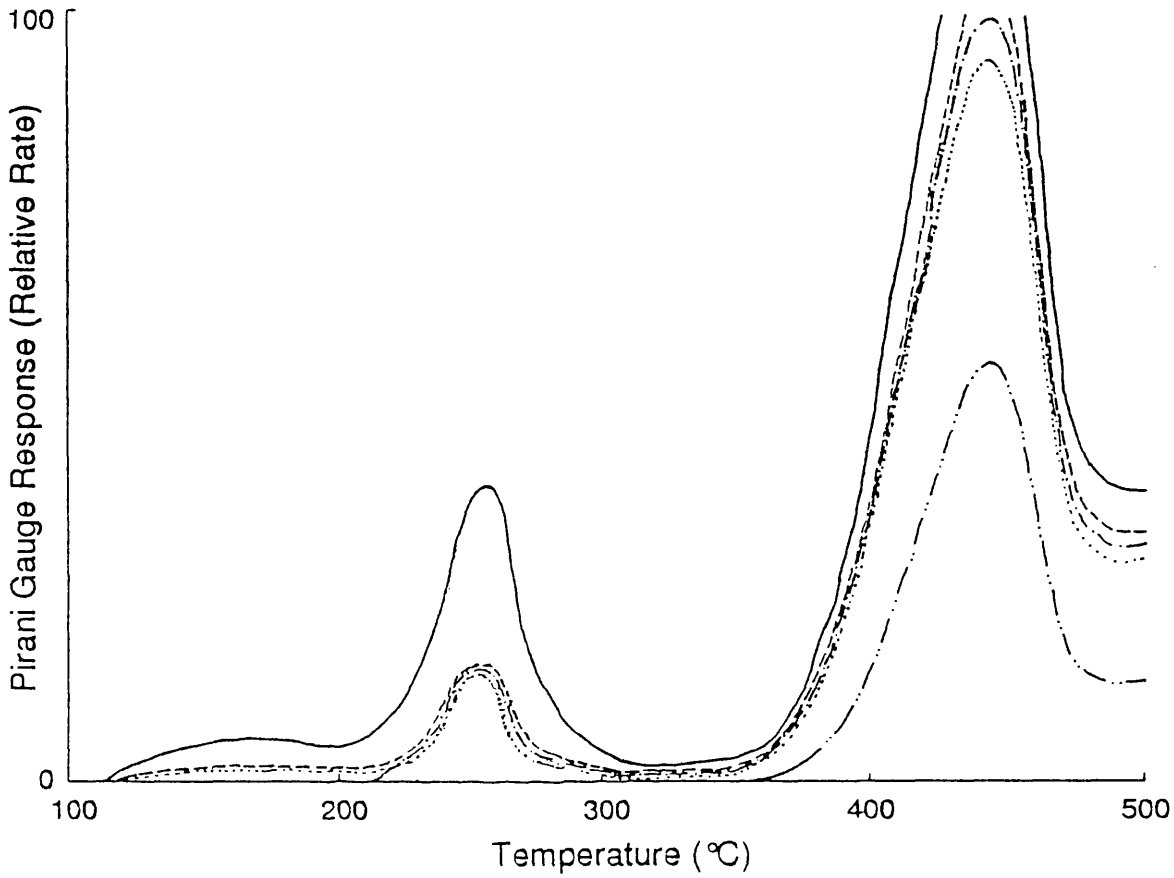


Fig. 5.2 DSC curve for PMAA sample obtained at heating rate 10°C/min under nitrogen flow.



Key

——————— 0℃
— — — — — -45℃
- - - - - - - — -75℃
— - — - — - -100℃
— - - — - - - -196℃

Fig. 5.3 TVA curve for PMAAA sample heated in vacuum to 500°C at 10°C/min.

TABLE 5.2 TVA, DTG, TG and DSC data for PMAA

TVA		DTG		TG	DSC	
Temp. range °C	Peak temp. °C	Temp. range °C	Peak temp. °C	% weight loss for stage	Temp. range °C	Peak temp. °C
200-280	228	200-285	340	18	190-275	230
350-500	420	350-480	425	70	350-475	455

The TVA curve for the PMAA presented in Fig. 5.3 shows two stages of polymer breakdown. The first stage, between 200 and 280°C, is followed by a large peak in the temperature region 375 to 500°C. Below 200°C there is slow release of volatile material, due to absorbed water in the polymer.

In the first stage of degradation at around 200°C, the curve shows simultaneous evolution of the main volatile product of the stage (water) along with a small amount of CO_2. The Pirani response for the 0°C trap is caused by both products but water vapour condenses in the -45, -75 and -100°C traps giving Pirani responses due to only CO_2.

Over the temperature interval 280-350°C, the polymer is stable protected by the anhydride groups that have formed as a result of dehydration reactions.

In the second stage of degradation between 350 and 475°C, PMAA suffers extensive degradation in which anhydride groups formed in the first stage decompose with the elimination of CO_2 and CO. In this stage of degradation abundant backbone scission occurs towards higher temperatures which produces a small concentration of unsaturation (66). The TG curve also shows the largest weight loss (70%) in this temperature region. The TVA diagram shows increased levels of volatile products, including non-condensable gases (mainly CO and CH_4).

The main features of the TG, DTG, DSC and TVA data are summarised in Table 5.2.

At the end of the TVA experiment, the fractions of different volatility produced by the pyrolysis quantitatively determined by direct weighing are presented in Table 5.3. The major product fraction consists of cold ring fraction (tar), which is 45% of the original sample and is composed of products of rather high molecular weight. The tar is formed mainly in the second stage of degradation, when backbone scission is occurring.

Table 5.3 The material balance for the fractions collected during the degradation to 500°C of the poly (methacrylic acid) under TVA conditions.

No	Fraction	%
1	Condensable liquid of which	23.0
	water	9.20
1a	methacrylic acid	7.00
1b	Aliphatic Hydrocarbon	1.80
1c	Aromatic Hydrocarbon	3.20
1d	O containing Compounds	2.30
2	Cold ring fraction (tar)	45.45
3	Residue	3.25
4	Gases (non-condensable + C_2-C_4)	27.83
	Total	100.0

IDENTIFICATION OF DEGRADATION PRODUCTS

SUB-AMBIENT THERMAL VOLATILISATION ANALYSIS

Condensable volatile products from the TVA experiment were collected in a liquid nitrogen trap in the vacuum system and were separated by the SATVA method. The SATVA trace obtained for polymer is given in Fig. 5.4. Table 5.4 shows the products in the various degradation fractions. For the liquid fraction, only the more volatile products which are identified by IR spectroscopy and by on-line mass spectroscopy are listed.

The SATVA curve shows four main peaks. The first large peak is due to CO_2, from decomposition of anhydride. The second is due to a small quantity of isobutene, and the neighbouring very minute shoulder is due to some methanol. The third significant peak is mainly due to ether which was used as a precipitant in polymer purification. The gas phase IR spectra of the products at the first, second and third peaks are given in Fig. 5.5. The fourth large peak is mainly due to water and other fragmentation products of the polymer, a very small amount of methacrylic acid, traced by on-line mass spectroscopy, also distils at this peak.

The liquid fraction collected during the TVA experiment was also examined by the GC-MS technique after removing water and MAA. The concentration of the products in the analysed sample was determined by integrating the ion

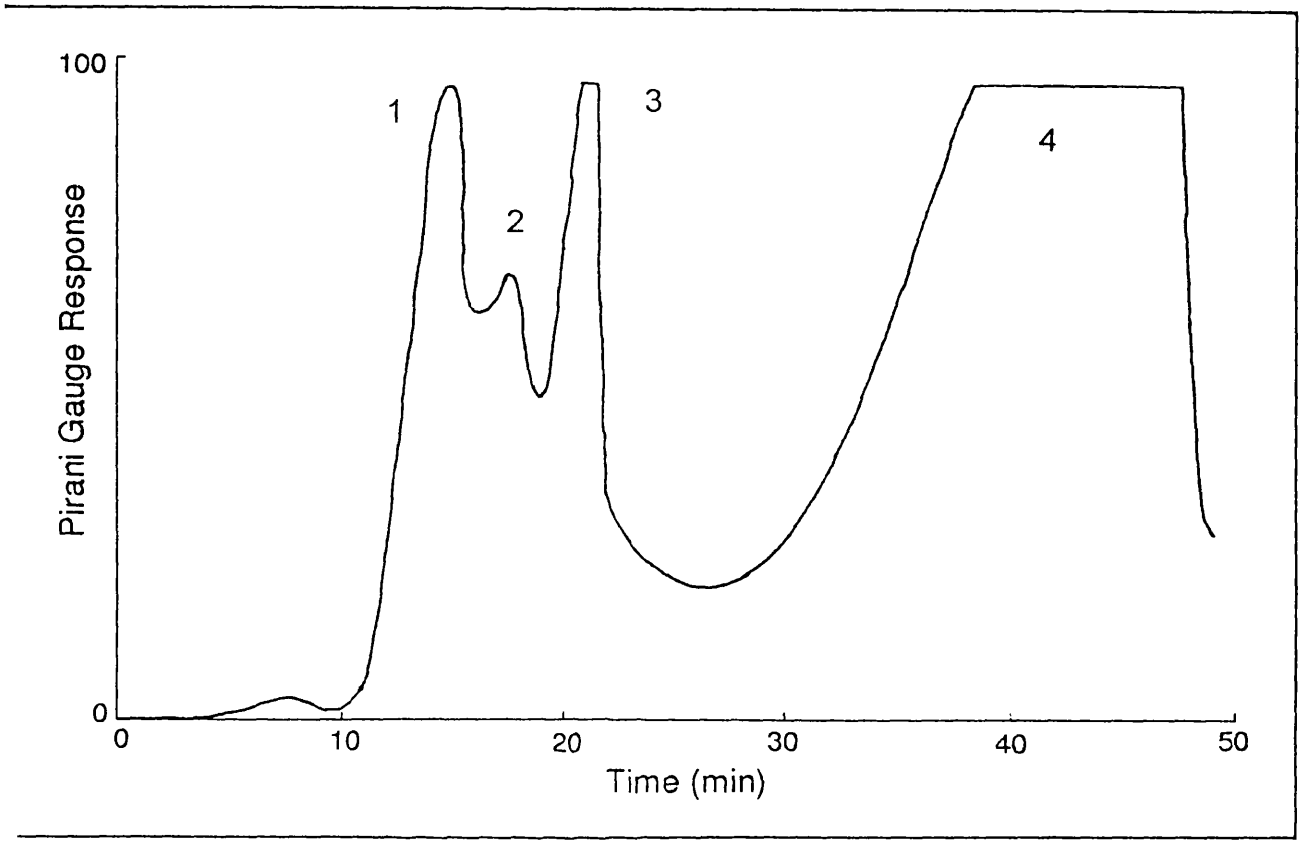


Fig. 5.4 SATVA curve of the degradation products, obtained under TVA conditions of PMAA sample.

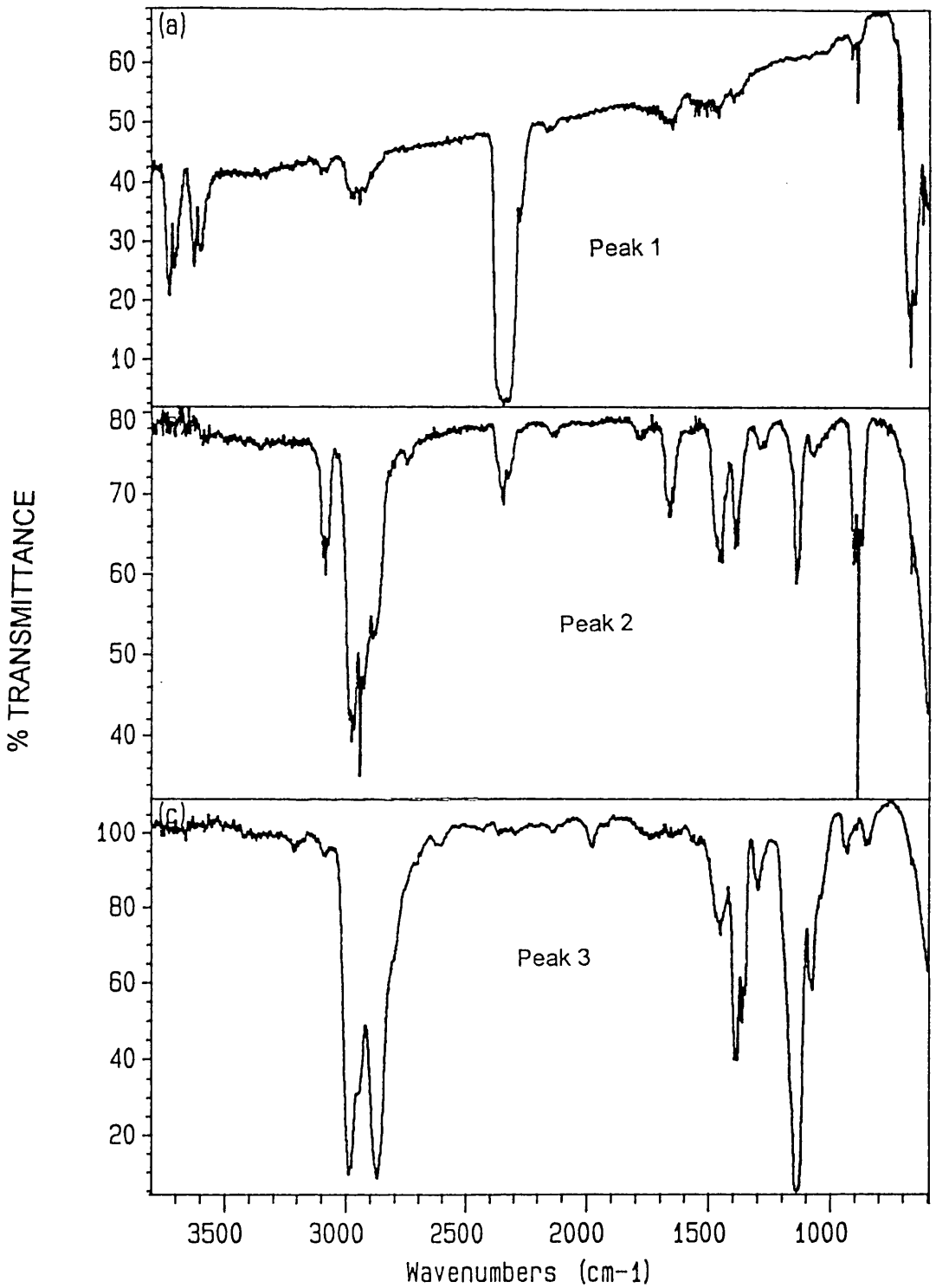


Fig. 5.5 Infrared spectra of the condensable gases and liquid fraction for degradation of PMAA to 500°C under TVA conditions.

current under the peaks. The products of liquid fraction are listed in Table 5.5.

The major products in the liquid fraction of PMAA are aromatic (43%) and oxygen-containing compounds (32%). PMAA gives a relatively high fraction of O-containing compounds in the liquid fraction and 1,3,5-trimethyl benzene as the major product.

Table 5.4. Products of the thermal degradation of PMAA to 500°C at 10°C/min, under vacuum established by the listed methods.

Noncondensable at -196°C	Condensable volatile Gases	Liq. Fraction	Cold ring fraction	Residue
MS only	IR & MS		IR MS & GC-MS	IR only
CO CH_4	CO_2 ethane propene isobutene	water methacrylic acid xylene, tri-methyl benzene ethylbenzene	aliphatic content anhydride groups α, β – unsaturated ketones some aromatic contents	black involatile residue with heavily substituted aromatic rings

Table 5.5 The composition of the liquid fraction collected during the pyrolysis of PMAA after the removal of water and methacrylic acid

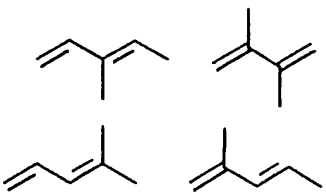
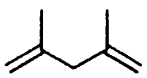
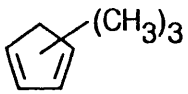
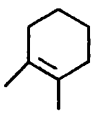
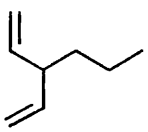
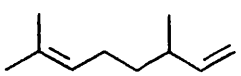
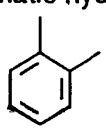
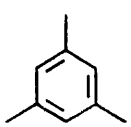
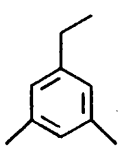
	Compound	MW	%
	Aliphatic hydrocarbons		
1		82	2·2
2		96	4·5
3		108	1·2
4		110	7·3
5		110	1·0
6		138	1·5
	Other Aliphatic[a]	—	7·0
	Total Aliphatic	—	24·7
	Aromatic hydrocarbons		
7		106	1·6
8		12	24·6
9		134	1·1

Table 5.5 (continued)

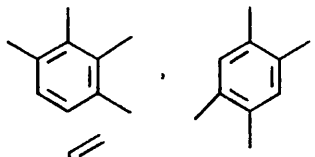
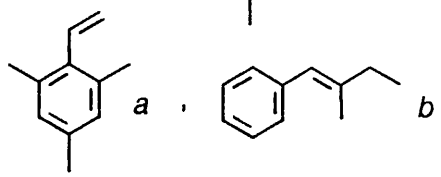
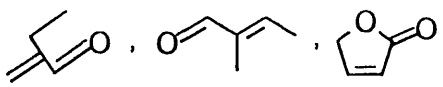
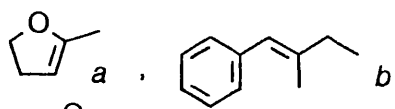
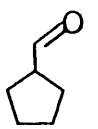
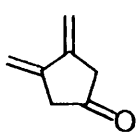
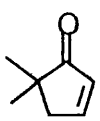
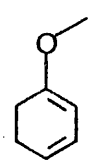
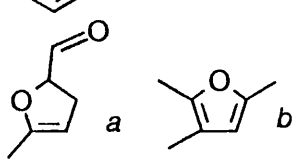
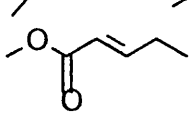
	Compound	MW	%
10		134	9·2
11		146	0·9
	Other Aromatic[a]	—	6·0
	Total Aromatic	—	43·4
	Oxygen containing compounds		
12	CH_3COOH	60	1·6
13		84	2·5
14		96	1·0
15		98	0·5
		—	43·4
16		108	5·9
17		110	0·4
18		110	1·3
19		110	1·6
20		114	4·5

Table 5. 5 (continued)

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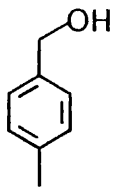
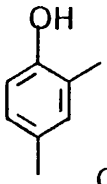
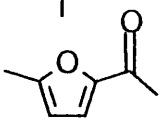
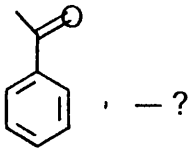
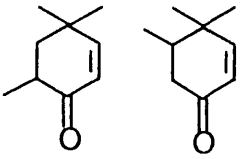
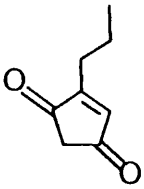
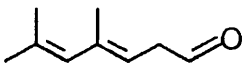
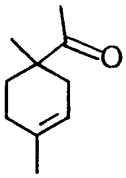
21		122	0·6
22		122	0·9
23		124	0·5
24		134	2·4
25		138	0·4
26		138	3·6
27		138	0·5
28		152	1·0
	Others [a]	—	2·7
	Total O containing compounds	—	31·9
	Total general		100·0

[a] Under 0.5% each

COLD RING FRACTION

The cold ring fraction products condensed on the upper part of the degradation tube were removed after the experiment with a volatile solvent and transferred to a weighed glass sample tube. After evaporation of the solvent at room temperature, the weight of cold ring fraction was determined. This fraction was examined by IR spectroscopy and by mass spectrometry, using a probe heated to 220 and 330°C. The mass spectra of the CRF given in (Fig. 5.6a-b), indicate that a mixture of materials is produced at these temperatures.

The CRF, which is the major product fraction accounting to 45% of the original sample, is mainly formed in the second stage of degradation. The CRF is composed mainly of products of high molecular weight with boiling points over 250°C.

The IR spectrum of the CRF is compared in (Fig. 5.7b) with the spectrum of the undegraded copolymer (Fig. 5.7a).

The main features of the CRF spectrum are the aliphatic content, seen through the absorption bands (2973-2870, 1380 cm^{-1}), and anhydride groups, through the absorption bands 1803, 1765 and 1130 $cm.^{-1}$ The CRF spectrum also shows a strong absorption band at 1703 cm^{-1} with overtone above 3200 cm^{-1} which is attributable to α,β–unsaturated ketone which is formed by decomposition of anhydride rings at higher temperature. There is also a little unsaturation present at 1645 $cm.^{-1}$ Aromatic contents which are significant in the liquid fraction (Table 5.5) are only present in CRF in small quantities. These can be seen through the bands at 2993, 1610,1450, 930, 900, 730 $cm.^{-1}$

The structure of the tar is almost identical to the one shown by the polymer heated at temperatures between 380-400°C which confirms that it consists of large polymer breakdown fragments.

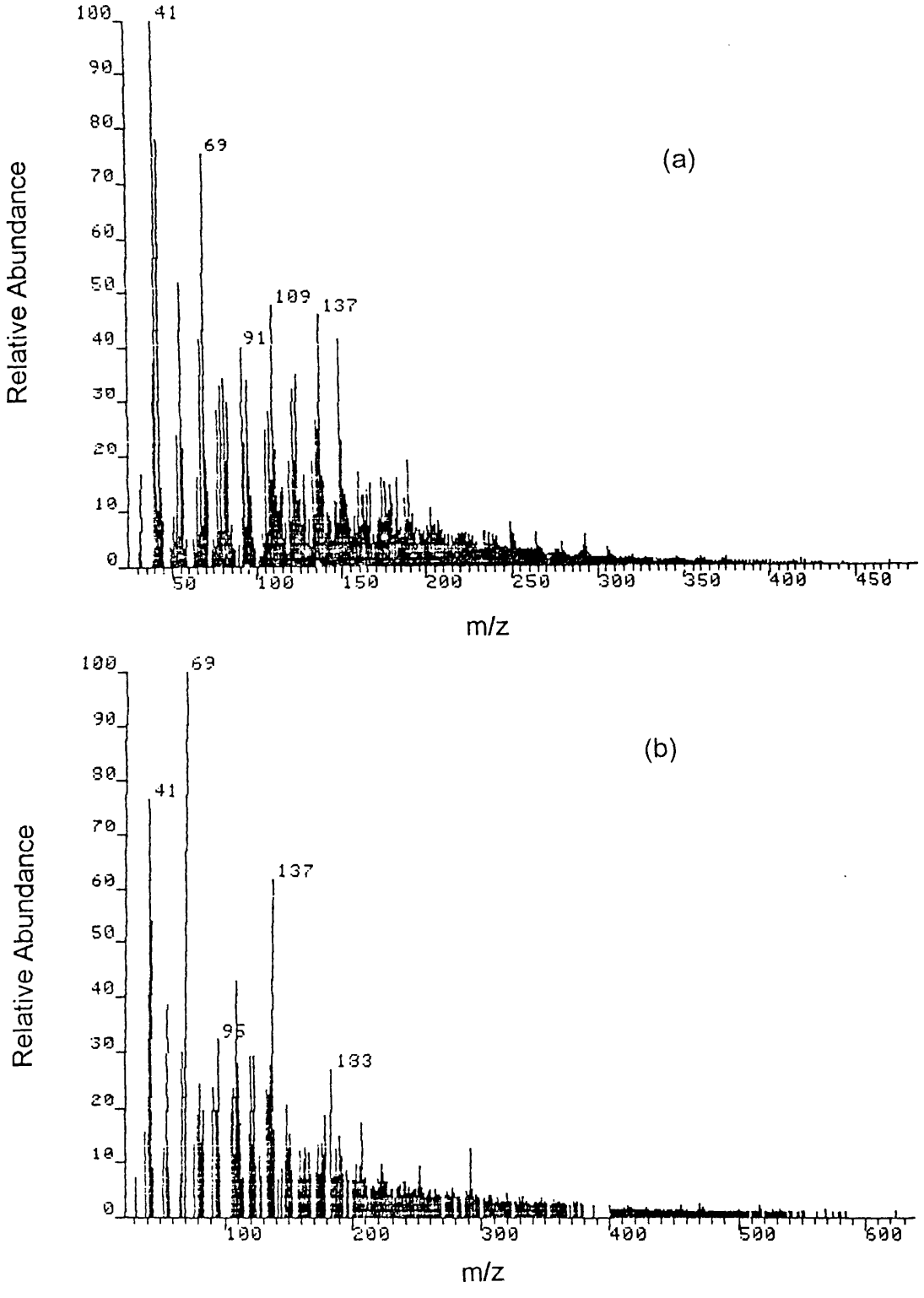


Fig. 5.6 Mass spectra of cold ring fraction (CRF) from the degradation of PMAA to 500°C under TVA conditions using probe temperatures of (a) 220°C (b) 330°C.

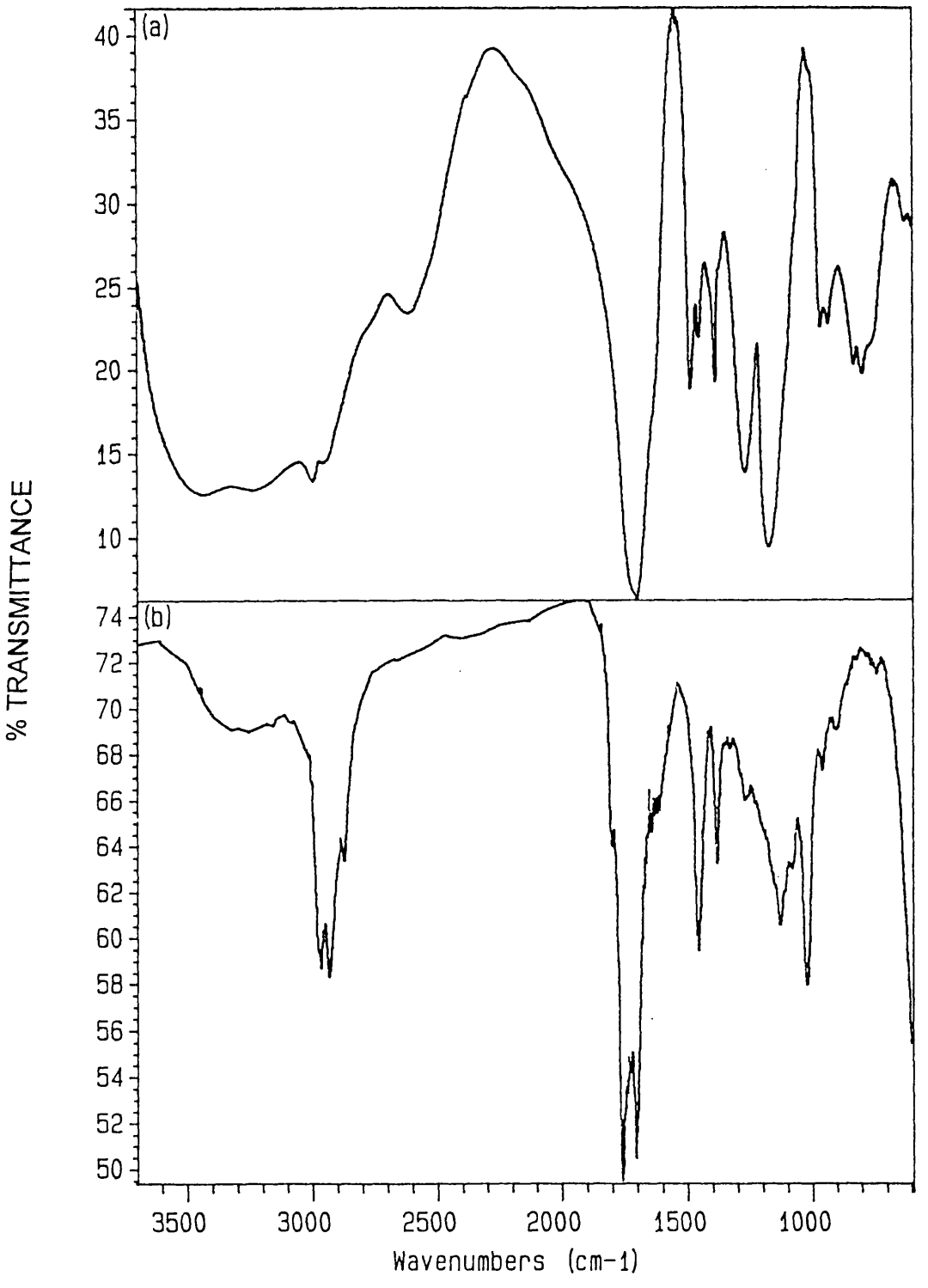


Fig. 5.7 IR spectra of (a) undegraded copolymer (b) cold ring fraction of PMAA degraded to 500°C under TVA conditions.

FTIR-SPECTROSCOPIC INVESTIGATION OF STRUCTURAL CHANGES DURING THE DEGRADATION OF PMAA

The structural changes in the PMAA during the thermal degradation have been investigated by FTIR reflection absorption spectroscopy using a film cast on stainless steel plate.

In a typical temperature-programmed experiment the changes in the polymer structure were followed by heating the polymer film at a rate of 10°C/min to different temperatures up to 500°C. FTIR spectra of film cooled after heating to desired temperature were measured using reflection-absorption apparatus. In some cases diffuse reflectance spectra were obtained which were subjected to automatic deconvolution.

Undegraded PMAA presents the following bands of interest (Fig. 5.8a) : a large ν_sC=O band centred at 1700 cm^{-1} characteristic to the COOH dimer resulting from hydrogen bond association. It has its corresponding νOH, a large band stretching on both sides of the peak at 3245 $cm.^{-1}$ There is another peak in this region, at 3435 cm^{-1} which can hardly be seen, but which comes out upon deconvolution. It corresponds to some water molecules associated with the COOH groups which could not be removed by moderate drying. Extensive drying was not attempted due to the risk of anhydrisation. Other bands due to the acid dimer can be found in the fingerprint region: 1400, 1270, 930-965 cm^{-1} (split). The first two bands are combinations of the in-plane O—H bending and C—O stretching coupled in the dimer. The bands at 930-965 cm^{-1} are due to the OH out of plane bending in the dimer. The bands appearing at 1175 and 830-800 cm^{-1} have not been identified, although they have been attributed to acids in solid state. In this work they disappear through anhydrisation, so there is reason to believe that they are also related to the combined vibrations in the COOH dimer.

The presence of COOH and water molecule associations, in addition to those of the COOH dimer, could be the reason for the broadening of the 1700 cm^{-1} band and for the splitting of the 930 and 800 cm^{-1} bands.

Heating PMAA to 200°C in a nonisothermal experiment brings about the formation of six-membered anhydride ring with peaks at 1804, 1750 and 1025 cm^{-1} (Fig. 5.8b), which is in agreement with previous work (28). The spectrum of the polymer heated to 240°C (Fig. 5.8c), shows that the carbonyl absorption band (νC=O) at 1750 cm^{-1} moves to 1765 cm^{-1} and the intensity ratio of the 1804 and 1765 cm^{-1} bands increases, demonstrating that a great number of anhydride links are now intermolecular. At this temperature there is also a small change in intensity and shift of the CH_3 group absorbance from 1450 to 1466 cm^{-1} as a result of their increased rigidity upon anhydride formation. The solubility tests show the polymer becomes insoluble after heating to 240°C, due to the formation of intermolecular anhydride links.

At 280°C (Fig. 5.8d) the formation of anhydride is abundant and few COOH groups are left isolated (monomeric absorption at 3550 cm^{-1}). The νC=O peaks at 1804 and 1765 cm^{-1} have increased with the ratio becoming almost 1:1, a sign of extensive intermolecular anhydride formation. The C—O—C band of the anhydride is wide covering the region 1200-1030 $cm.^{-1}$ New, small absorption bands appear at 1657, 1620, 1570 $cm.^{-1}$ The last two bands, corroborated by the strong band at 1460 cm^{-1} and the bands at 870 and 740 cm^{-1} show that aromatic rings begin to form. With PMAA heated up to temperatures in the range 300-400°C FTIR spectra show constant decay of the anhydride groups. The formation of an aromatic structure, monitored by the increase of the peak at 1600 $cm,^{-1}$ takes place in a narrow temperature interval, between 400 and 420°C. At 420°C (Fig. 5.8e) the anhydride rings have almost disappeared and the aromatic system is extended. The aromatic rings show only 1H atom vibration (870 cm^{-1}), hence are pentasubstituted. CH_3 groups are substituents of the aromatic rings as results in the shift of the ν_a CH_3 from 2986 to 2966 $cm.^{-1}$ Ketone groups (ν C=O, 1706 cm^{-1}) conjugated with double bonds are situated on a hydrocarbon chain.

At 440°C the spectrum is that of a char (Fig. 5.8f). A large aromatic system (see the band in the 1500-1600 cm^{-1} region), strongly substituted (no bands in the fingerprint region) is the main characteristic. A hydrocarbon chain is associated with it. Ketone groups are found on the hydrocarbon chain, (1740 cm^{-1}), indicating some conjugation with unsaturation (1706 cm^{-1}).

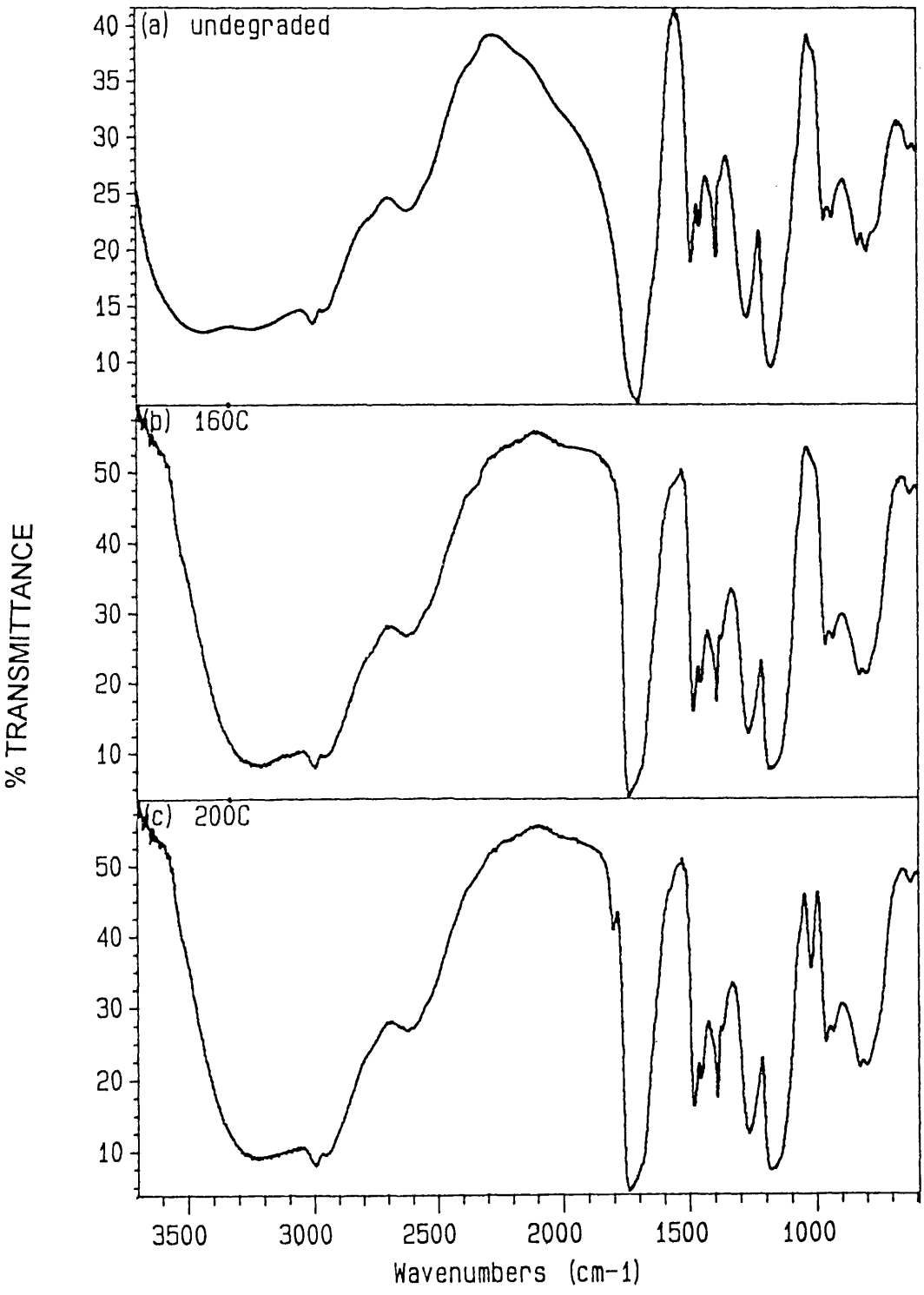


Fig. 5.8 Infrared spectra of PMAA: (a) before and after heating in vacuum to: (b) 160°C (c) 200°C.

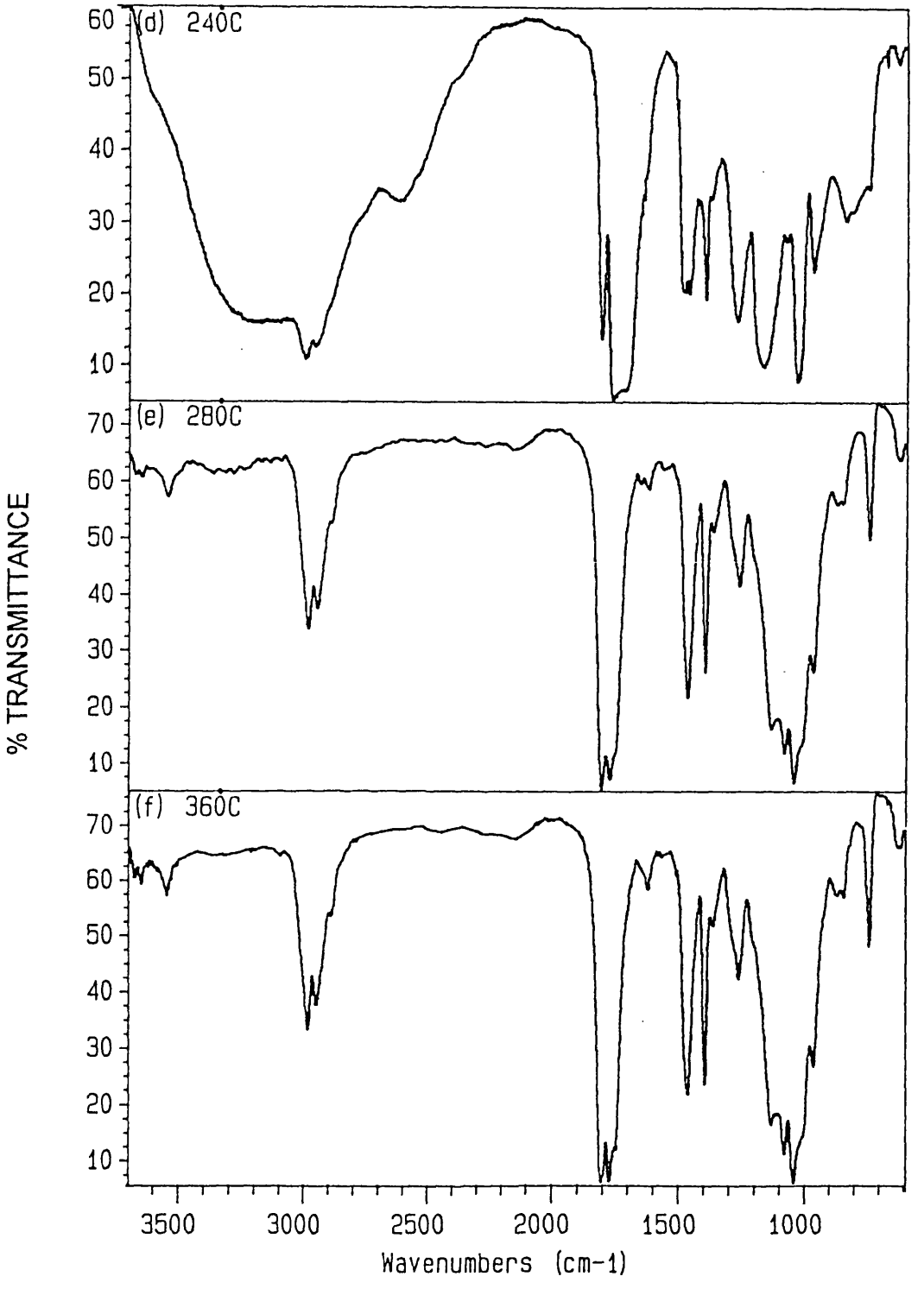


Fig. 5.8 Continued (d) 240°C (e) 280°C (f) 360°C.

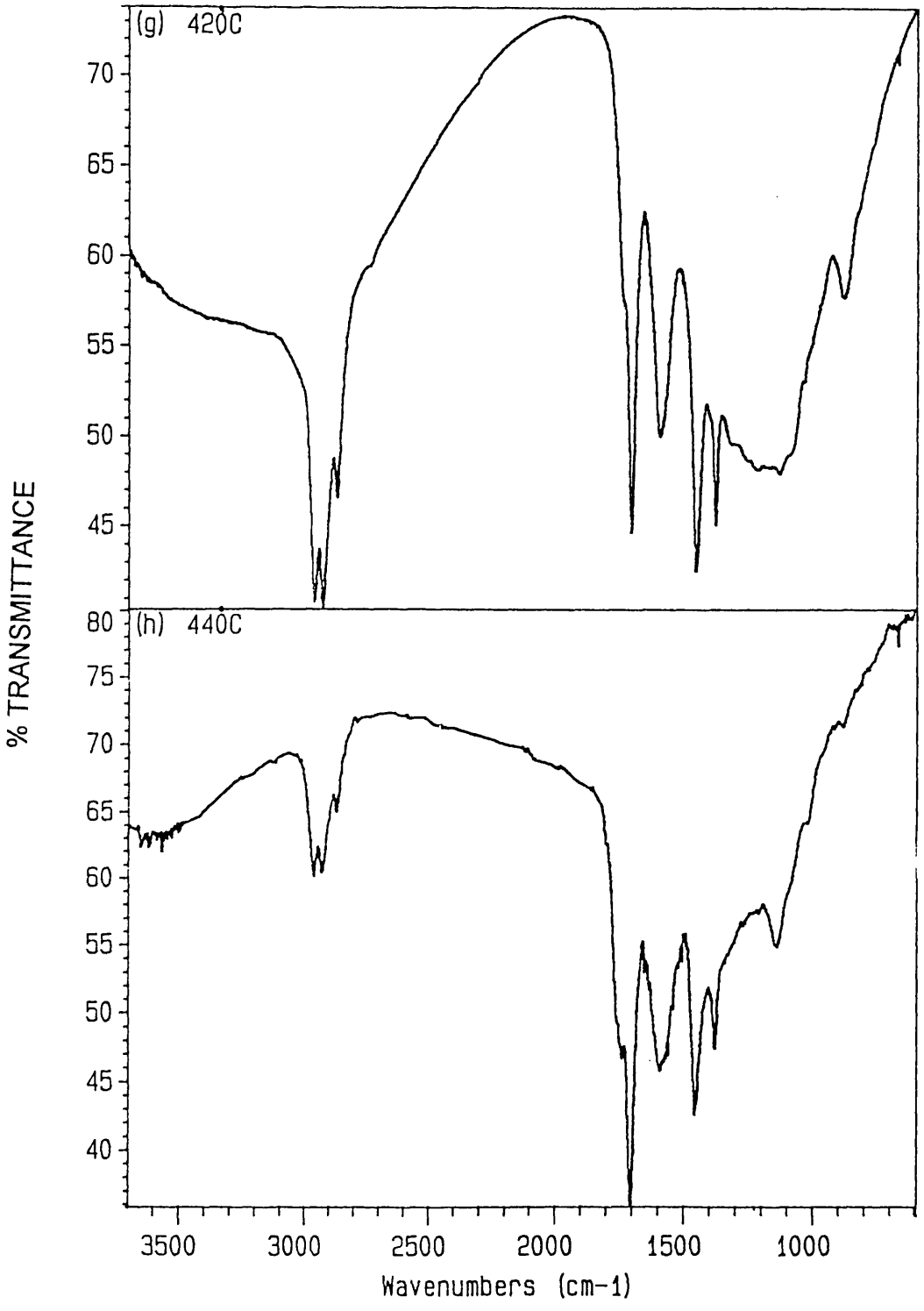


Fig. 5.8 Continued (g) 420°C (h) 440°C.

At 480°C the polymer becomes too black for a spectrum to be measured.

Fig. 5.9 shows the transformations of the spectra in the 3100-3000 and 1657-1500 cm^{-1} regions where the appearance of unsaturation and aromatic structure can be followed over the temperature interval 280-440°C. At 420°C, the formed rings are isolated, a "loose" aromatic structure being characteristic. At 440°C the isolated rings condense, with a shoulder appearing at 1570 cm^{-1}, characteristic of condensed rings. There are no definite peaks in the region 3000- 3100 $cm,^{-1}$ but a broadening of the base of the main C—H stretch peak, possibly obscuring unsaturated and aromatic C—H stretch, can be observed after 420°C.

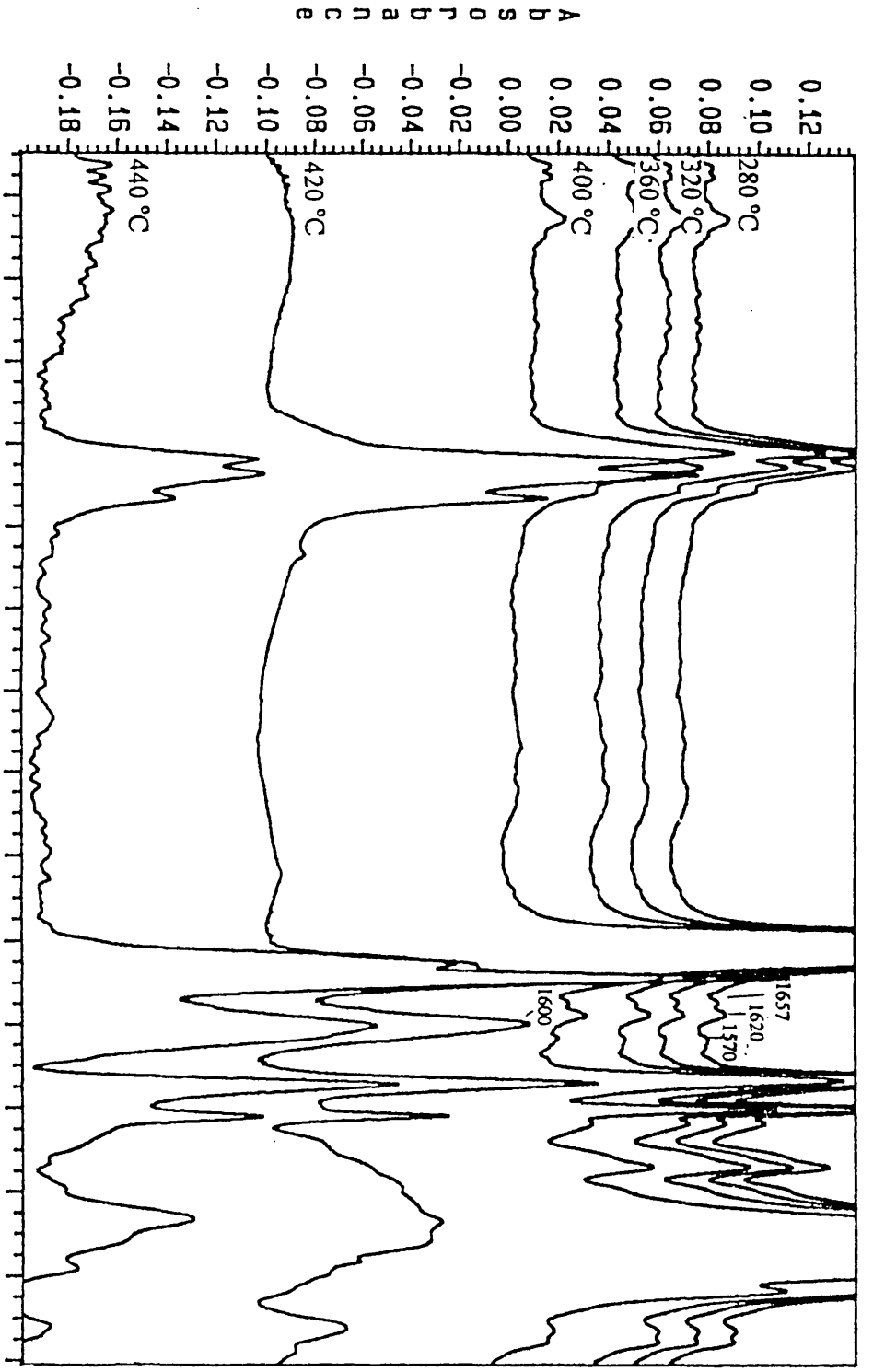


Fig. 5.9 FT-IR spectra of thermally degraded PMAA obtained by

DISCUSSION

PMAA shows two stages of degradation. In the first stage, between 200-300°C the majority of the COOH groups eliminate water and form anhydride. A small fraction of COOH groups decarboxylate and a very small fraction of the PMAA units depolymerise (79,80).

PMAA produces a high fraction of tar (45%) and significant fractions of gases (28%) and liquids (23%), shown in Table 5.3

The TG curve (Fig. 5.2) shows that the weight loss of 18% in the first stage of degradation is due to water, CO_2 and methacrylic acid formation through the above processes. The liquid products collected in this stage (water and MAA) account for 16%, hence 2% weight loss is due to CO_2. Consequently, 4% of the polymer loses its COOH groups by decarboxylation. A simple calculation from the material balance and ion integration of GC-MS results shows that 88% of the polymer gives anhydride and 8% depolymerises. Table 5.3 gives the estimated amount of water and MAA formed/100g polymer through the above processes. Water and methacrylic acid constitute the major part of the liquid fraction collected during pyrolysis. The rest of the liquid fraction (7.3%) has a composition which will be considered at a later stage of the discussion.

Between 300 and 350°C, the polymer is stable. In a second stage of degradation, between 350 and 500°C, the anhydride decomposes with chain scission and forms a high fraction of tar (45 %), containing products with MW > 200. The tar is formed at the beginning of the second stage and consists of large fragments of the polymer structure existing at around 400°C : an aliphatic chain carrying anhydride groups, α,β–unsaturated ketones formed through the decomposition of some anhydride groups and a few aromatic rings which are isolated (non-condensed) and fully substituted.

Scheme 1 tries explain the observed transformation of the PMAA. The anhydrisation reaction starts at 200°C and continues over the whole temperature range up to 280°C. At 200°C anhydride formation is intra

molecular, but soon intermolecular anhydride groups are formed which result in the reduced solubility of the polymer after heating to 250°C. Above 280°C PMAA is another polymer, now poly(anhydromethacrylic acid).

The anhydride has a rigid structure, due to the CH_3 branches. The biradical intermediate (I) formed through its decomposition has a high probability of splitting and forming end chain unsaturation (reaction 1). The scission occurs at random, the presence of anhydride rings in the tar demonstrating this. A number of anhydride rings, however, will decompose as in reaction (2) leading to the formation of the α,β–unsaturated ketone. Intramolecular anhydride links decompose in a similar fashion (reaction 3). The carbonyl radical (III) has an increased probability of recombination with another radical, generating an α, β–unsaturated ketone as in reaction (3).

The intermolecular anhydride rings can also explain the formation of aromatic structures after 400°C as a result of the extensive decomposition of the anhydride links and from very little preceding unsaturation, as it appears from the FTIR spectra. The mass decomposition of the intermolecular anhydride creates biradicals in a position which is favourable to 6-membered ring formation (reaction 4). The excited intermediate (IV) will break some bonds setting it partly free, but still keeping with the polymer. Such reactions of normally lower probability occur with increased probability towards 420°C when the polymer has lost 50% of its initial weight and the resulting char has a more compact structure.

The liquid and gas fraction is mainly formed in the second stage of degradation. As the temperature rises in this stage, the decomposition of the anhydride groups becomes more intense yielding products with small molecular weight (< 200) which constitutes a liquid and gas fraction. The "true" liquid fraction remaining after the subtraction of water and methacrylic acid is low (7.3%) and the gas fraction is appreciable (28%) showing intense fragmentation. The detailed composition of the liquid fraction without water and methacrylic acid is given in Table 5.5 as % relative to the total weight of the liquid fraction. Although the liquid fraction is not a major fraction, the identification of its components is important for it offers indications about the pyrolysis mechanism of the poly (anhydromethacrylic acid).

The main hydrocarbon component is 1,3,5-trimethylbenzene (Table 5.5), which alone accounts for 25% of the liquid fraction and for 2% of the decomposed polymer. Its formation can easily be predicted from the simultaneous decomposition of two successive anhydride rings.

Products like 11b, Table 5.5, show that methyl branches are sometimes lost with the formation of double bonds. Products like 10 cannot be explained unless admitting the addition of CH_3 radicals to unsaturation.

If anhydride rings decompose with the elimination of CO_2 alone (reaction 6, *Scheme 2*) the biradical intermediate (II) can initiate several other reactions. It can suffer scission forming the carbonyl radical (VI) (reaction 7) which can give the attack on a double bond closing a ring of 5 or 6 C atoms and producing cyclic ketones such as products 17, 25, 26, Table 5.5. Reaction (8) illustrates this type of reaction with the formation of product 17.

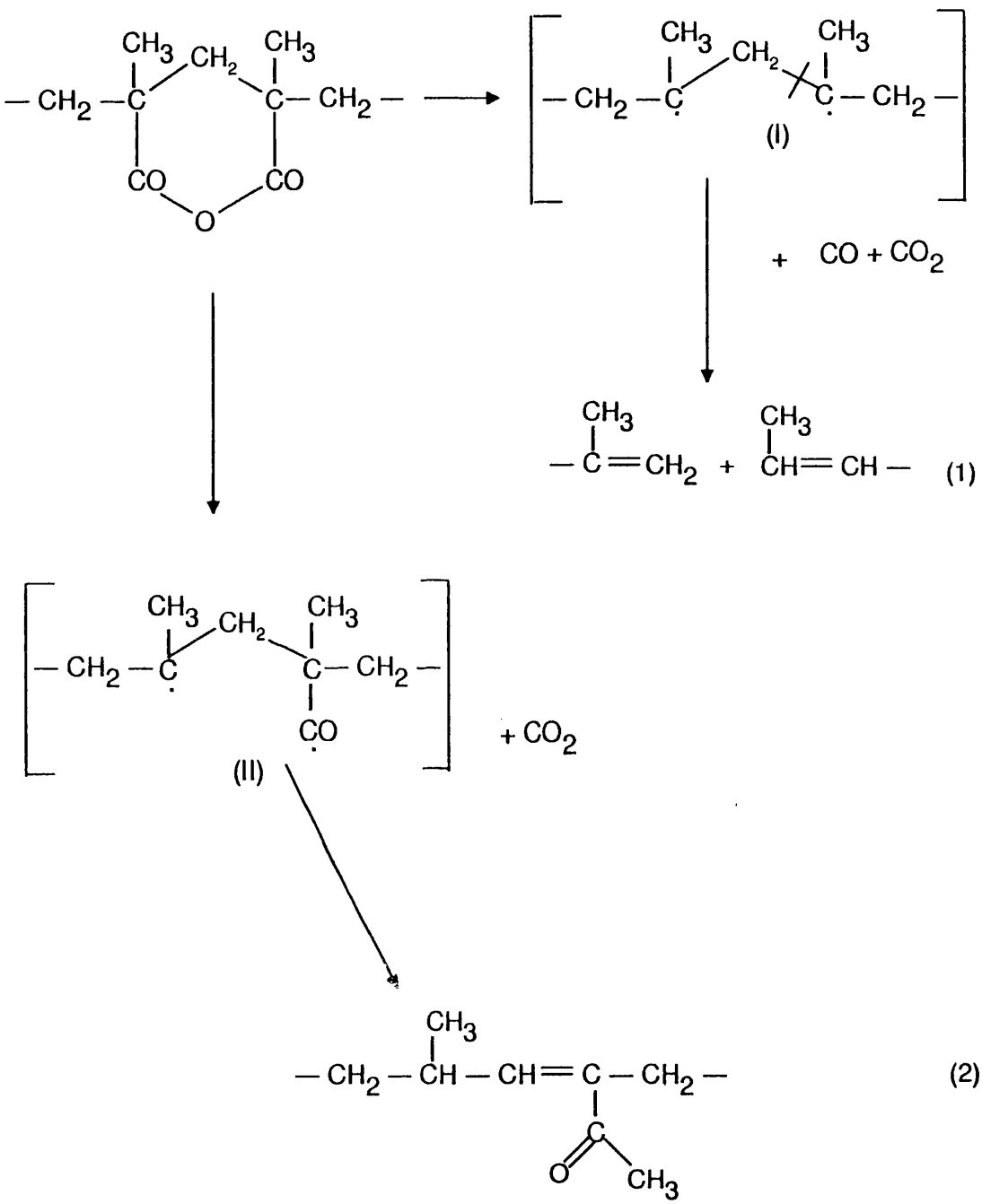
In products like 15, 24 and 28, the biradical (II) has recombined with H or methyl radical at the carbonyl site and formed a double bond at the tertiary alkyl site. The closing of rings is due to the attack of an aliphatic radical formed 5 or 6 C atoms away on a double bond situated α,β to the C=O group.

The carbonyl biradical (II) can rearrange as in reaction (9) producing the alkenoxy radical (VII) which can attack a double bond closing a ring of 5 or 6 C atoms and producing cyclic ethers such as in reaction (10) leading to compound 19b. Products 14, 19, 23 in Table 5.5 are formed through this type of reaction.

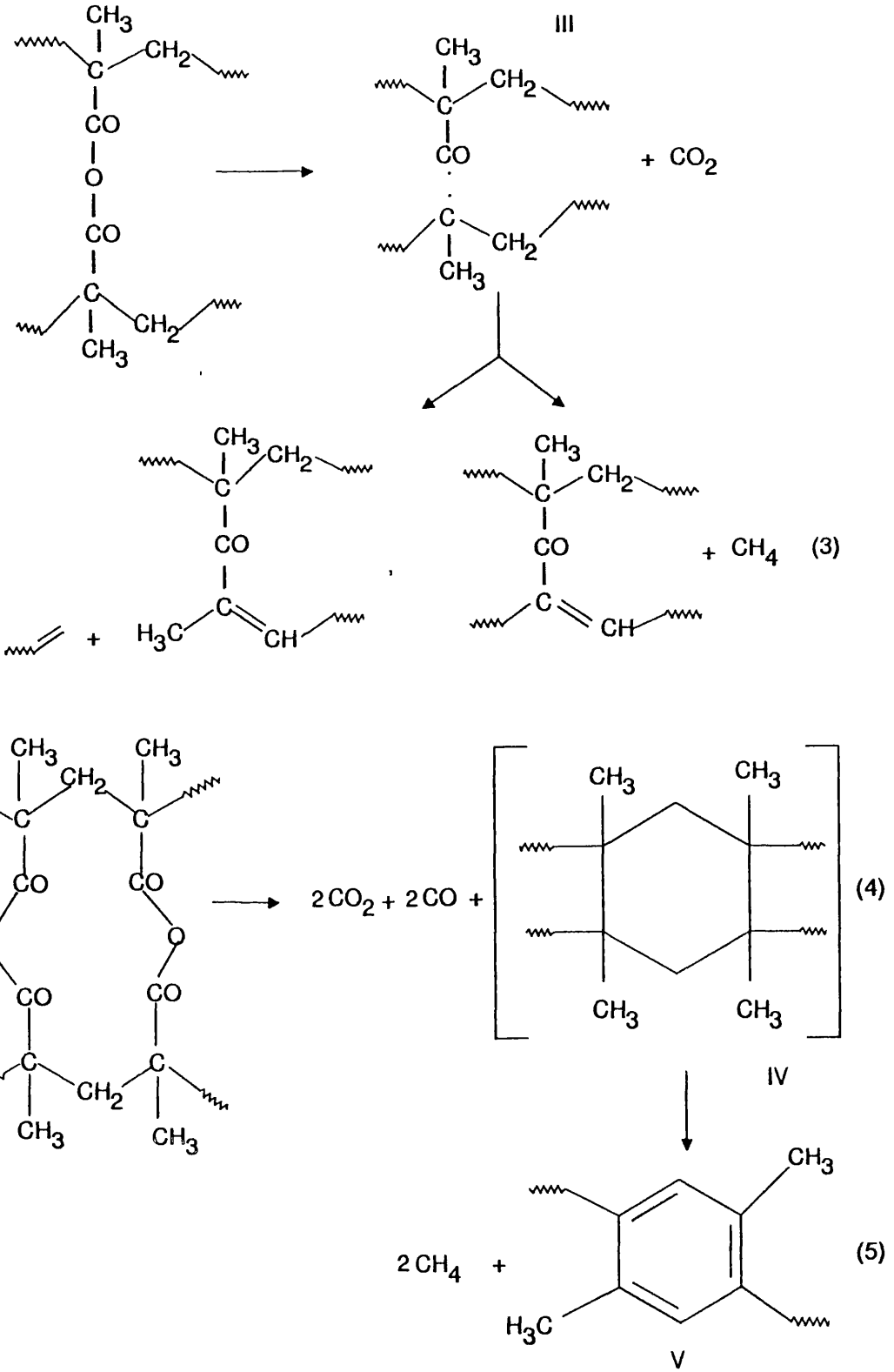
The general trend which distinguishes PMAA from PVA is the formation of 1,3,5-trimethylbenzene as the major compound and a relatively high fraction of O-containing compounds in the liquid fraction. The main O-containing products formed by the breakdown of anhydride rings are ketones, esters and cyclic ethers.

Mechanism for thermal degradation of PMAA

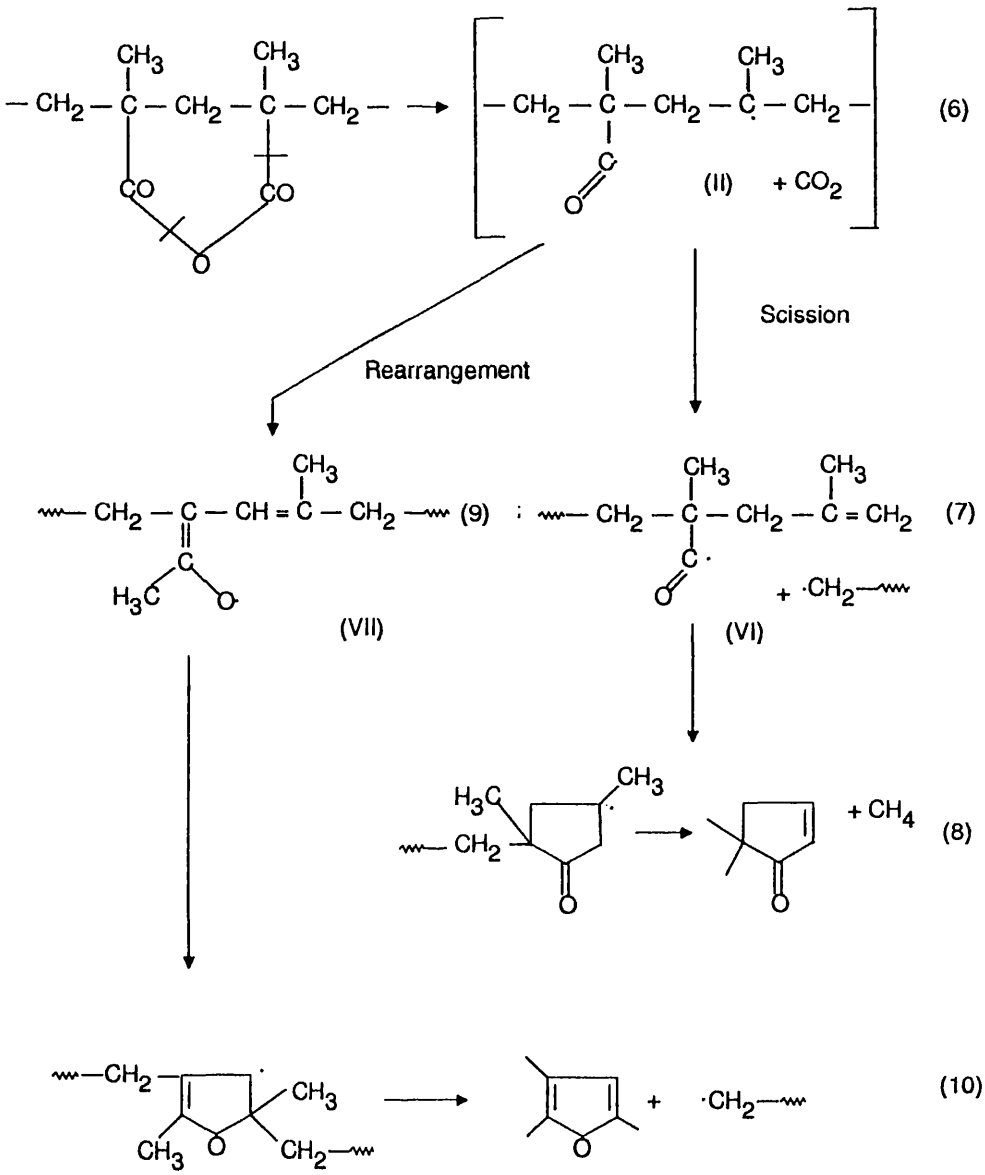
Scheme 1



Scheme 1 Continued



Scheme 2



The FTIR spectroscopy studies show that in PVA crosslinking develops through the unsaturation and PMAA also crosslinks, but through the anhydride links.

CONCLUSION

PMAA shows two degradation stages. In the first stage, between 200 and 280°C the major part of the COOH groups (88%) eliminate water and form intra- and inter molecular anhydride links. A small fraction of the COOH groups (8%) suffer depolymerisation to methacrylic acid, and 4% decarboxylate.

In the second stage of the degradation, between 350 and 500°C, the anhydride decomposes at random giving large scission fragments which constitute tar. The structure of the tar consists of a largely aliphatic chain carrying anhydride groups, α,β–unsaturated ketones and few aromatic rings. A hypotheses for the formation of the aromatic rings through the decomposition of intermolecular anhydride links has been advanced.

PMAA decomposes to large tar fraction (45%), moderate liquid and gas fraction (around 25%) and a residue of only 3%. The gas fraction is the largest in the studied polymers. The analysis of the liquid fraction gives indications about the breakdown pathways of the anhydride groups. The main reaction route is the elimination of CO and CO_2 and formation of the hydrocarbons, of which 1,3,5-trimethylbenzene is the most representative compound. Other breakdown pathways yield O-containing compounds.

CHAPTER SIX

THE THERMAL DEGRADATION BEHAVIOUR OF THE METHACRYLIC ACID-VINYL ACETATE COPOLYMER

Copolymers of methacrylic acid with various monomers such as styrene and methyl methacrylate have been subject of many investigations. These copolymers are commercially useful: for example the copolymer of methacrylic acid with styrene is used in desalination, paper substitute technology and carpet shampooing. However, the copolymer of methacrylic acid with vinyl acetate (VA—MAA) has never been studied previously.

To understand the pyrolysis behaviour of VA—MAA copolymer the corresponding homopolymers were studied in detail and are described in previous Chapters (4&5). The presence of comonomer may either stabilise or destabilise the copolymer relative to the homopolymer. For instance, methacrylic acid - methyl methacrylate copolymer is much more stable than MMA homopolymer as anhydride structures are formed which effectively stabilise the copolymer by inhibiting the unzipping of MMA units (78).

In the present studies a VA—MAA copolymer was synthesised such that it contained a large proportion of alternating VA and MAA units. The purification of monomers and polymerisation methods are described in Chapter 3 and the preparation conditions are summarised in Table 6.1.

The thermal stability of the VA—MAA copolymer was investigated by using well known degradation techniques, i.e. TVA, TG and DSC, under programmed heating up to 500°C in nitrogen and vacuum conditions.

Table 6.1 Preparation conditions for the vinyl acetate—methacrylic acid copolymer made by free radical polymerisation

Amount of methacrylic acid	1.44 g
Amount of vinyl acetate	65.8 g
Amount of initiator (AIBN)	1%*
Time of polymerisation	2 hours
Temperature of polymerisation	70°C
Conversion	3%

* Relative to the total weight of monomers

The various fractions from TVA (cold ring, liquid fraction, residue) were collected and weighed for material balance after pyrolysis.

The composition of the liquid fraction was determined using GC-MS by integrating the ion current under the peaks of the different compounds. The structural changes in the copolymer during the degradation were investigated under continuous evacuation at temperatures up to 500°C in isothermal and programmed heating experiments.

Envisaged structure of the VA—MAA copolymer

VA and MAA do not give a totally alternating copolymer, due to the fact that although $r_1 = 0.01$ (VA) which is effectively close to zero and $r_2 = 20$ (MAA) is very large (see Chapter 3). However, the feed chosen gives a copolymer that contains a high proportion of alternating sequences, and in which the MAA units are mainly isolated. This greatly reduces the possibility of intramolecular anhydrisation. According to the statistical model (74,81) if the above ratio of monomers in the feed had been maintained during the synthesis then about 65% of the copolymer would be alternating and 35% would consist of 2-4 unit sequences of either monomer. Instead, the MAA concentration in the copolymerisation system was allowed to deplete during the reaction, thereby reducing the number of MAA sequences. However, the monomer ratio (VA:MAA) in the copolymer was still close to 1 (53:47) as shown by the intensity ratio of the FTIR peaks corresponding to O—C = O ester (1740 cm^{-1}) and acid (1705 cm^{-1}) (66).

THERMAL DEGRADATION

THERMOGRAVIMETRIC ANALYSIS (TG)

The thermogravimetric (TG) and differential thermogravimetric (DTG) curves for VA—MAA copolymer were obtained under dynamic nitrogen flow at a heating rate of 10°C/min up to 500°C.

The curves, VA—MAA reproduced in Fig. 6.1, show that the thermal breakdown of the copolymer occurs in three stages. The weight loss in the temperature region 200 to 300°C is 25%, in which the most important reaction is a dehydration reaction of adjacent MAA units, which leads to anhydride formation, as in PMAA, and causes a rate maximum at 280°C. The weight loss 25%, is much more than what would be expected for anhydride formation. The reason for the higher weight loss is the overlapping of the next stage, which begins at 280°C (as can be seen from IR spectrum (Fig. 6.10c)), i.e. lactone formation with the elimination of acetic acid between adjacent VA and MAA groups.

This stage overlaps with the next, from 300 to 350 °C with rate maximum at 320°C, which in turn also merges with the third stage. The most important reaction in the second stage is lactone formation with the elimination of acetic acid between adjacent VA and MAA groups. The weight loss observed in this stage of degradation is 25%.

However, the total weight loss in the first two stages up to 350°C of 50%, is more than would be expected if all the available acid and ester units reacted to give lactone. This weight loss cannot be explained except by admitting that some anhydride rings decompose as the lactone is formed.

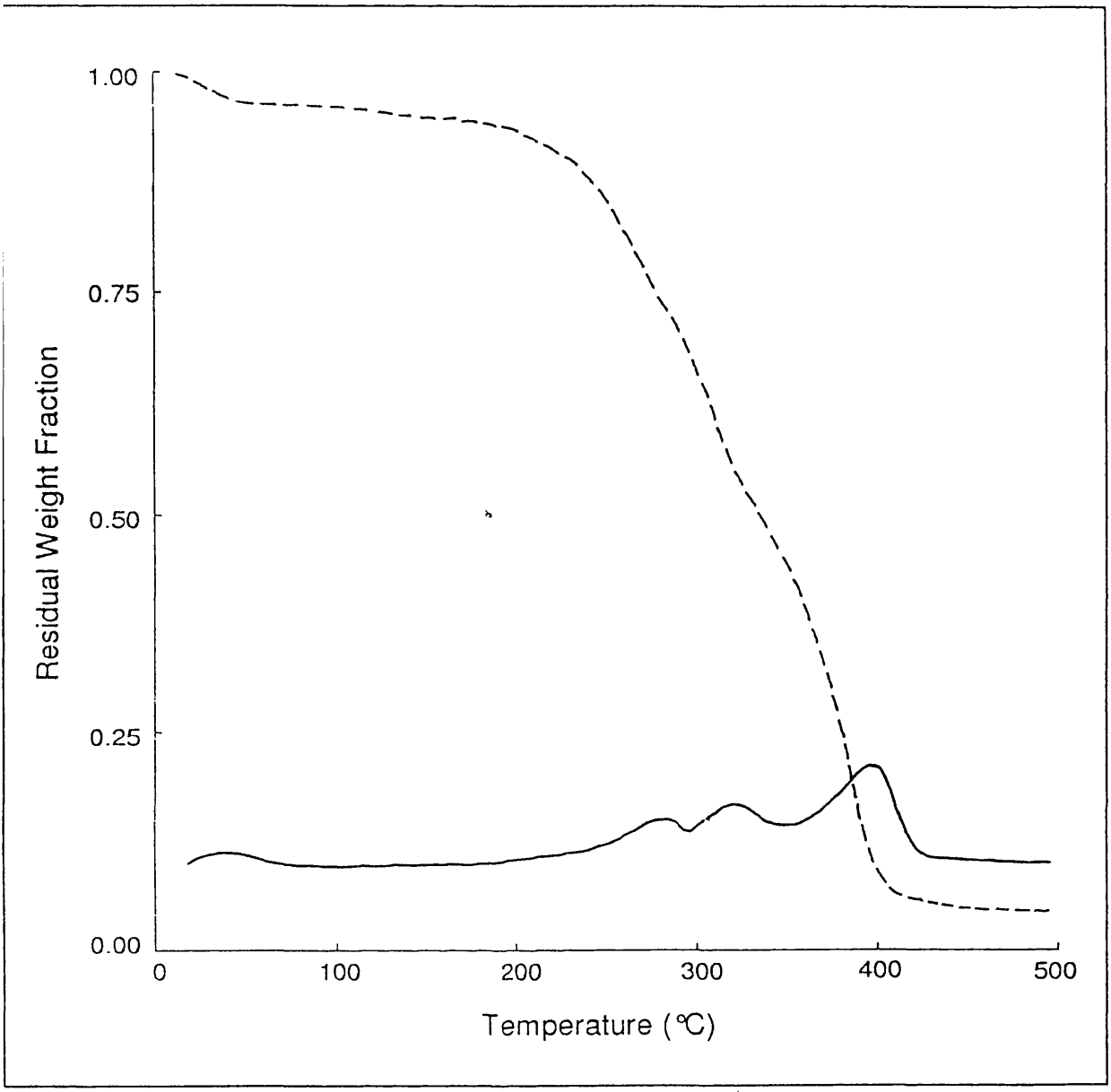


Fig. 6.1 TG and DTG curves for VA—MAA copolymer (heating rate 10°C/min nitrogen flow)

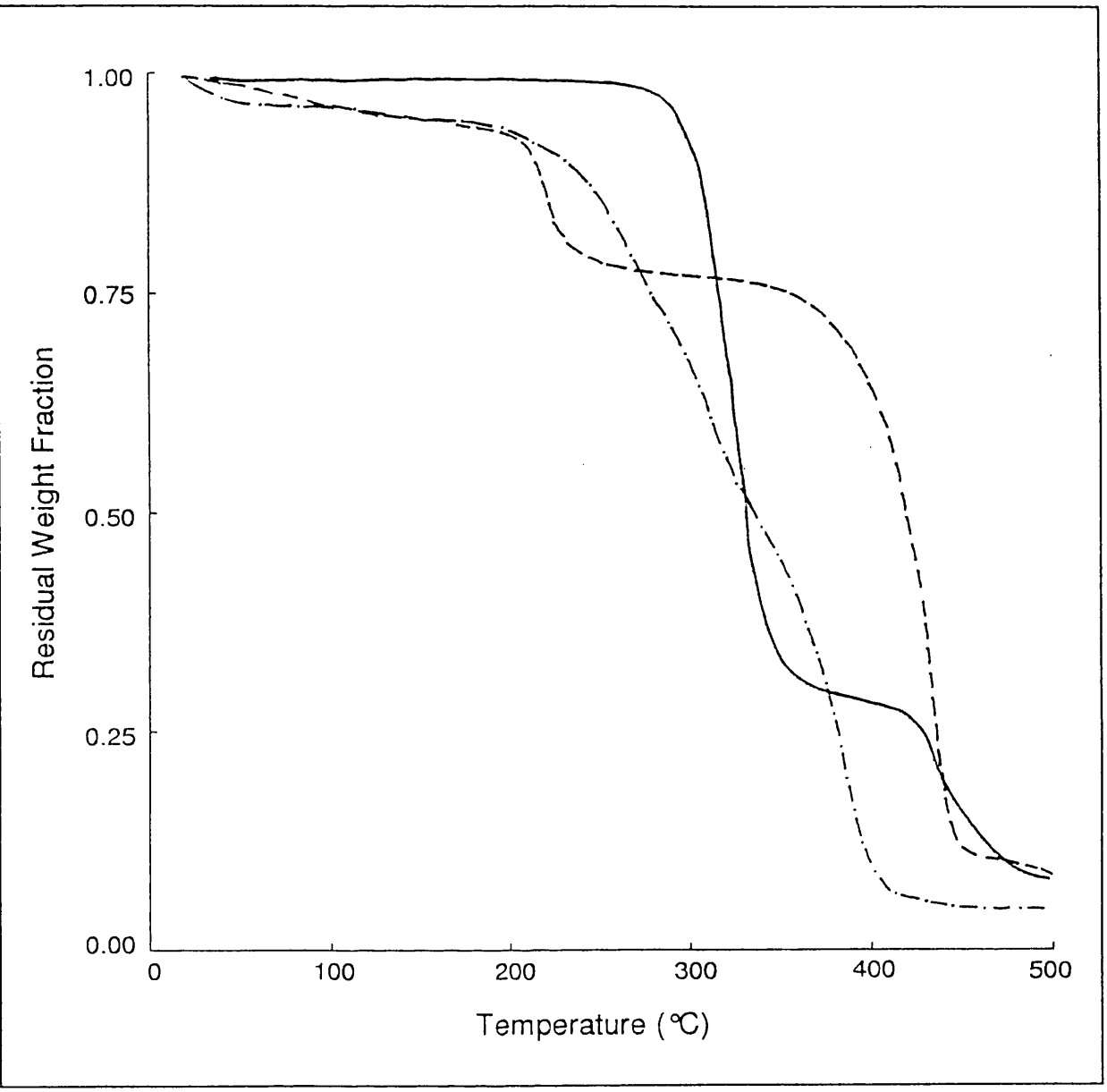


Fig. 6.2 TG curves (heating rate 10°C/min, nitrogen flow) for various polymers.

Key : (——) PVA, (------) PMAA, (— · — · —), VA—MAA copolymer

Table 6.2 TGA data for three polymers degraded in dynamic N_2 atmosphere.

% weight loss					
PVA		**PMAA**		**VA—MAA copolymer**	
Temperature region	Wt. Loss	Temperature region	Wt. Loss	Temperature region	Wt. Loss
260-375°C	70	200-285°C	18	200-300°C	25
375-500°C	20	350-480°C	70	300-350°C	25
----	---	----	---	350-430°C	47
Residue	9	Residue	3.25	Residue	3

PVA Poly(vinyl acetate)

PMAA Poly(methacrylic acid)

VA—MAA Vinyl acetate—Methacrylic acid copolymer

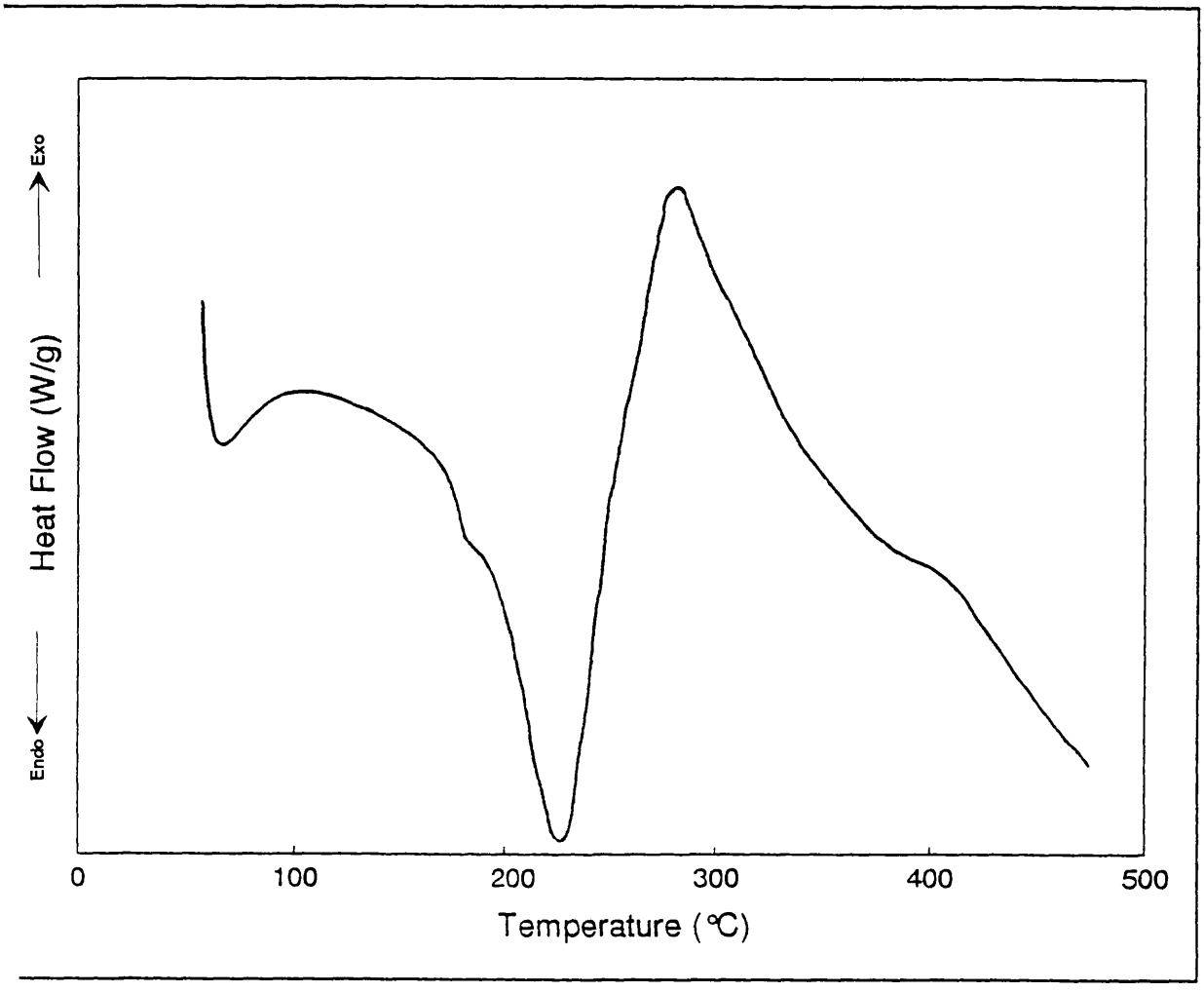
It appears that formation of the lactone induces strain in the macromolecular chain which results in the early decomposition of the anhydride. This makes up the third stage of the degradation, between 350 and 430°C with rate maximum at 390°C, which occurs at a lower temperature than the corresponding PMAA peak for anhydride decomposition.

The TG curves of three polymers; PVA, PMAA and VA—MAA are shown together in Fig. 6.2 to facilitate the comparison of the thermal behaviour. The % weight loss for each stage for all three polymers is presented in Table 6.2. The VA—MAA copolymer has a more continuous decomposition compared to its parent homopolymers. It also attains almost complete decomposition much earlier i.e. 425°C instead of 475°C for the homopolymers.

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The DSC trace for the VA—MAA copolymer is reproduced in Fig. 6.3. The DSC trace provides information on the thermal effects involved in the degradation stages, and confirms their temperature ranges.

The DSC curve shows a single deep endotherm in the temperature region 190 to 290°C, with the rate maximum at 230°C. This endotherm is associated with weight loss observed in the first stage of degradation in the TG curve. It is also in the same temperature range in which the dehydration peak of PMAA has been observed by TVA (Fig. 5.3). Above 290°C, the DSC curve of the VA—MAA copolymer shows a continuous decrease in the heat capacity as the polymer "evaporates" by conversion to volatile products, and the remaining char develops aromatic content.



ig. 6.3 DSC curve for VA—MAA copolymer (heating rate 10°C/min under nitrogen flow).

THERMAL VOLATILISATION ANALYSIS (TVA)

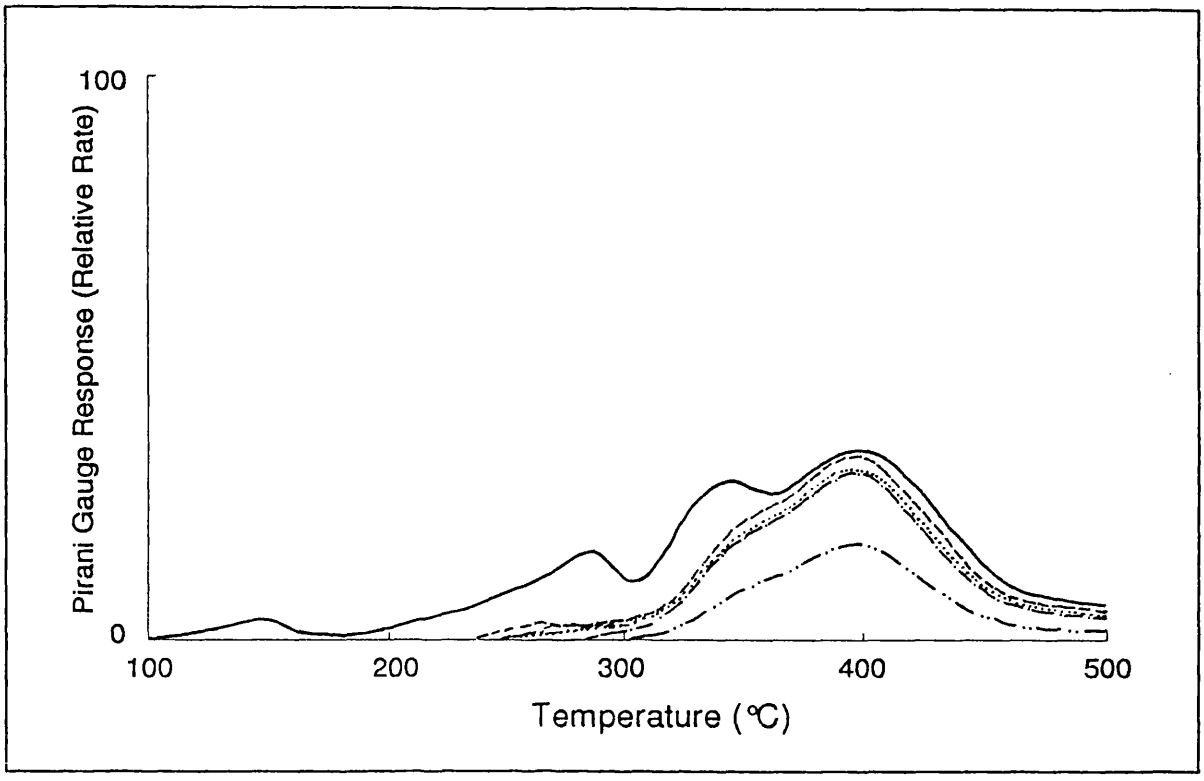
The VA—MAA copolymer was degraded to 500°C in a TVA experiment under continuous evacuation using a programmed heating rate of 10°C/min to 500°C. The TVA curve is reproduced in Fig. 6. 4.

The TVA curve shows three overlapping degradation stages. The results obtained from the TVA are consistent with the results obtained by TG analysis.

In the first stage of degradation, between 200 and 300°C, the Pirani gauge after the 0°C trap shows a larger pressure reading than the other traps due to water vapour. The -45° and -75° traces are slightly above the baseline but are still quite coincident indicating that a small amount of material produced in this temperature region is not condensed in these traps. The water produced in this temperature region is caused by the anhydrisation reaction between adjacent COOH groups. The IR spectra of partially degraded copolymer up to 300°C also confirms that anhydrisation is the only transformation.

The second stage of degradation which merges with the third stage is between 300 to 360°C with a rate maximum at around 330°C. The main product is acetic acid formed through reaction of adjacent VA and MAA units to give lactone rings. The TVA curve also shows the formation of some more volatile products including non-condensable gases.

The third and main stage of degradation is between 350 and 430°C with the rate maximum around 405°C. The pressure readings obtained on the Pirani gauges show higher responses for all traps.



Key

————	0°C
— — — — —	-45°C
- - - - - - - —	-75°C
— - — - — - —	-100°C
— - - — - - -	-196°C

Fig. 6.4 TVA curve for VA—MAA copolymer sample heated in vacuum to 500°C at 10°C/min.

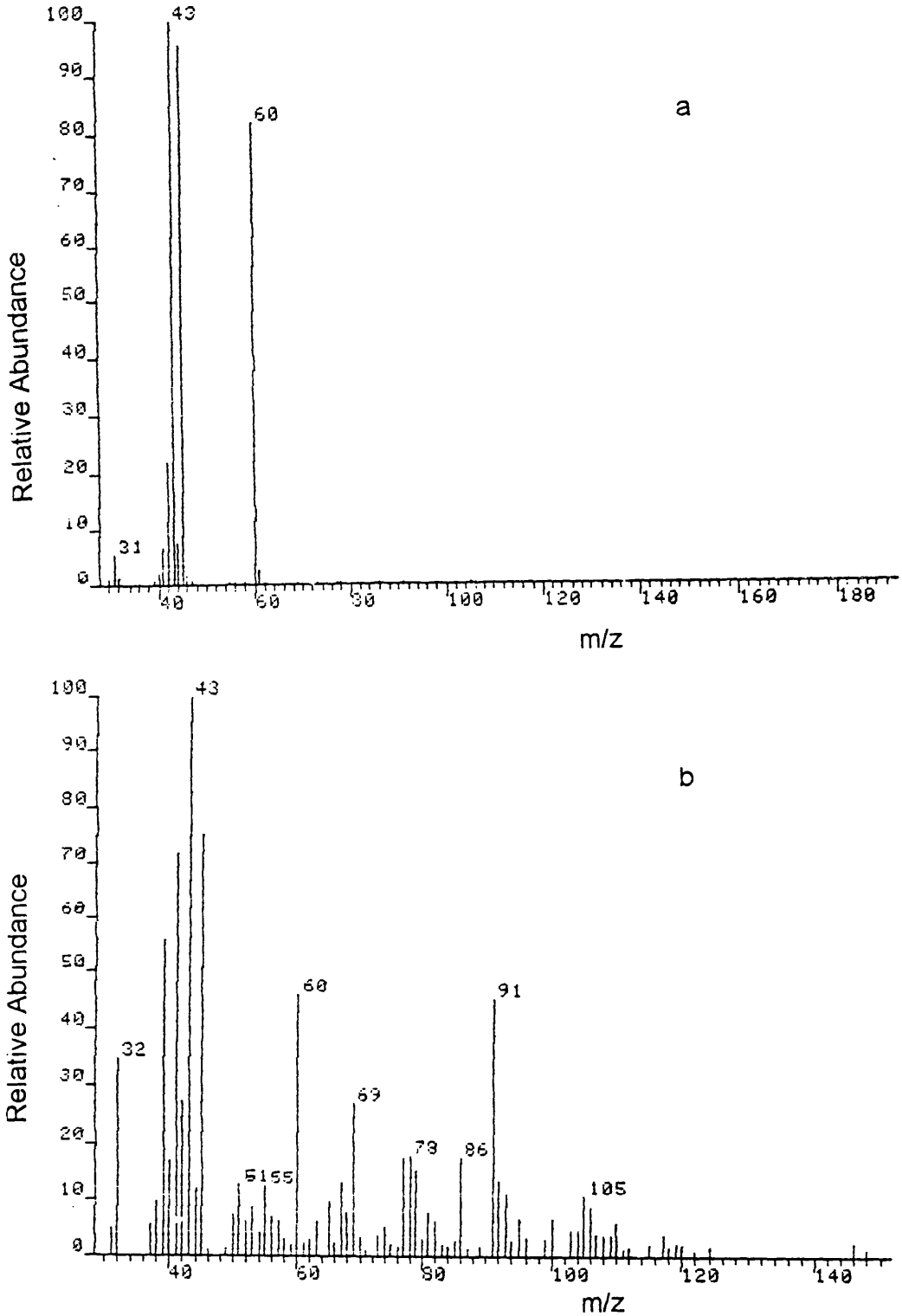


Fig. 6.5 Mass spectroscopic results of products collected from the degradation of VA—MAA copolymer in temperature regions, (a) 280-360°C (b) 360-500°C.

In this stage, the anhydride and lactone groups decompose extensively producing a large fraction of non-condensable gases (mainly CO) escaping through the -196°C trap. The reaction is displaced to lower temperatures than the corresponding PMAA peak for anhydride decomposition. The IR spectra of partially degraded copolymer show that the anhydride structures disappear quickly, and are virtually absent by 400°C. In the char, lactone groups survive up to 400°C, isolated between aromatic rings. At 480°C the last lactone groups disappear, giving way to the condensation of the aromatic rings in the strongly diminished char.

To identify the products at each of the three degradation stages shown in Fig. 6.4, another set of experiments was conducted, in which degradation products at each stage were collected separately and analysed by mass spectroscopy. The mass spectra of products collected from 280-360°C and from 360-500°C are presented in Fig. 6.5(a-b).

At the end of the experiment the fractions of different volatility were collected and determined quantitatively by direct weighing and are presented in Table 6.3. The products consist of condensable gases and liquids (48%), cold ring fraction (tar) (42.29%), non-condensable gases (9%) and very little residue (1%). The material balance for the PVA, PMAA and VA—MAA copolymer samples has been given in Table 6.4. The composition of the liquid fraction has also been given in Table 6.4 in the form of main classes of products, as was evaluated from the GC-MS chromatogram.

Table 6.3 Material balance of the fractions collected during the degradation to 500°C of the VA—MAA copolymer under TVA conditions.

No	Fraction	%
1	Condensable Liquids of which	
	water, acetic acid	} 39-43
1a	aliphatic hydrocarbon	
1b	aromatic hydrocarbon	} 5-9
1c	O-containing Compounds	
	Total liquid fraction	48
2	Cold Ring Fraction (tar)	42
3	Residue	1
4	Gases (non-condensable + C_2-C_4)	9
	Total	100

Table 6.4 Material balance of PVA, PMAA and VA—MAA copolymer after degradation to 500°C under TVA conditions.

		PVA	PMAA	VA—MAA
No	Fraction	%	%	%
1	Condensable liquids, of which	63.10	23.50	48%
	water	--	9.2	
	acetic Acid	59.80	--	} 39-43
	methacrylic acid	--	7.00	—
	aliphatic hydrocarbons	0.30	1.80	—
	aromatic hydrocarbons	2.80	3.20	} 5-9
	O-containing compounds	0.2	2.30	
2	Cold Ring Fraction (Tar)	42.29	45.45	19.00
3	Residue	0.98	3.25	8.10
4	Gases (noncondesable + C_2-C_4)	8.87	27.83	10.90
	Total	100.0	100.0	100.0

IDENTIFICATION OF DEGRADATION PRODUCTS

SUB-AMBIENT THERMAL VOLATILISATION ANALYSIS (SATVA)

The condensable gases and liquid collected during the degradation of the polymer in the TVA system were separated into their components by the SATVA method. Mass spectroscopic analysis was carried out during the SATVA separation by bleeding the products into the mass spectrometer. The condensable gases were analysed by IR spectroscopy.

The SATVA curve reproduced in Fig. 6.6 shows four peaks. The very small peak in the beginning is due to some aliphatic hydrocarbons. The first peak is mainly due to a larger fraction of CO_2. The material distilled at the second peak is mixture of products but is mainly methacrylic acid, methanol (solvent) and very small amount of ketene. The third peak which is of very small magnitude is due to hexane which was used as a precipitant. The fourth peak which is the main peak is mainly due to acetic acid, water and other fragmentation products.

The liquid fraction collected during the TVA experiment was also examined by the GC-MS technique. This could only be done after the major product, acetic acid, had been removed as it would damage the GC column and be retained in the MS, contaminating the other peaks. The concentrations of the other products in the analysed sample were determined by integrating the ion current under the peaks. The products analysed by GC-MS are presented in Table 6.5. The liquid fraction consisted of aromatic hydrocarbons, O—containing compounds and very little aliphatic hydrocarbons.

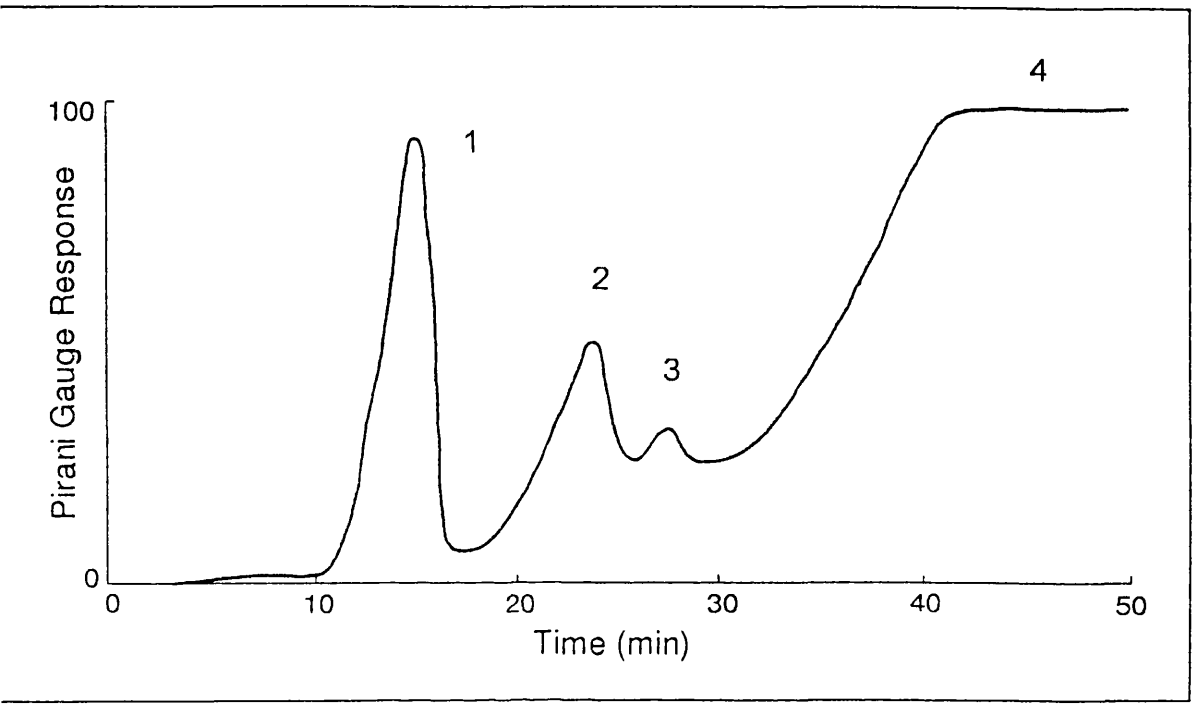


Fig. 6.6 SATVA separation of the condensable volatile degradation products from degradation under TVA conditions to 500°C for VA—MAA copolymer.

Table 6.5 The composition of the liquid fraction collected during the pyrolysis of VA—MAA copolymer (after removal of the major product acetic acid)

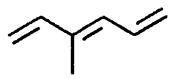
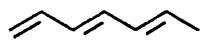
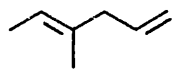
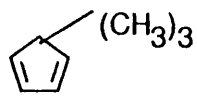
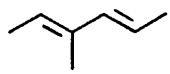
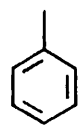
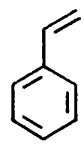
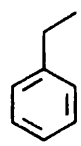
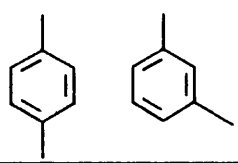
	Compound	MW	%
	Aliphatic hydrocarbons		
1		66	1·5
2		94	0·5
3		94	0·4
4		98	0·5
5		108	1·1
6		110	0·4
	Others[a]	—	—
	Total aliphatic hydrocarbons	—	6·7
	Aromatic hydrocarbons		
7		92	9·7
8		104	13·9
9		106	1·4
10		106	2·1

Table 6.5 (continued)

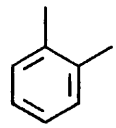
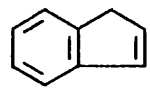
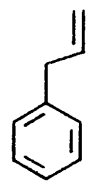
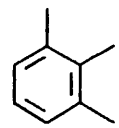
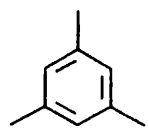
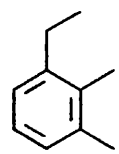
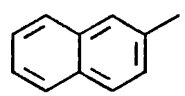
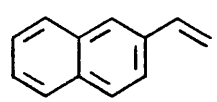
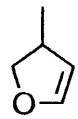
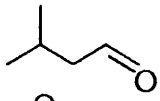
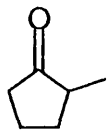
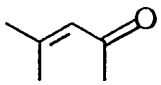
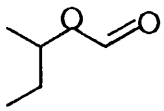
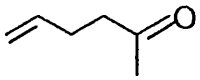
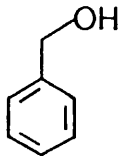
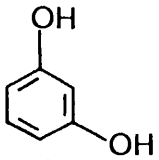
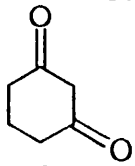
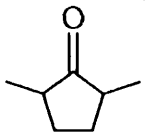
	Compound	MW	%
11		106	9·5
12		116	1·2
13		118	2·0
14		120	1·8
15		120	1·7
16		134	0·8
17		142	0·9
18		154	1·0
	Others [b]	—	18·9
	Total aromatic hydrocarbons	—	64·90

Table 6.5 (continued)

	Compound O-containing compounds	MW	%
19		84	0·20
20		86	0·40
21		98	1·75
23		98	1·00
24		100	0·50
25		100	2·30
26		108	2·30
27		110	5·60
28		112	2·75
29		112	1·46
	Others[a]	—	10·16
	Total O-containing compounds	—	28·20
	Total general		100·00

[a] Under 0.5% each

[b] Under 1.0% each

Table 6.6. Products of the thermal degradation of VA—MAA copolymer to 500°C at 10°C/min under TVA conditions established by the listed methods.

Noncondensable at -196°C	Condensable volatile		Cold ring fraction	Residue
	Gases	Liq. Fraction		
MS only	IR & MS		IR MS & GC-MS	IR only
CO CH_4	CO_2 ethane propene ketene	water acetic acid methacrylic acid toluene, xylene ethylbenzene	aliphatic content lactone groups α, β – unsaturated ketones some aromatic contents	black involatile residue with heavily substituted aromatic rings

Table 6.6 shows the products identified in the various degradation fractions. In case of the liquid fraction only the volatile products which were identified by IR spectroscopy are listed.

COLD RING FRACTION

The infrared spectrum of the light brown cold ring fraction (CRF) collected during the degradation of the VA—MAA copolymer to 500°C is presented in Fig. 6.7b. This fraction was examined by IR spectroscopy and by mass spectroscopy using a probe heated to different temperatures. It was also analysed by GC-MS. The IR spectrum of the undegraded copolymer is also presented for comparison in Fig. 6.7a, while the main absorption peaks are listed in Table 6.7.

The tar, which is 42% of the initial weight of the copolymer, is mainly formed towards the end of the second stage through the extensive decomposition of the anhydride groups. The IR spectrum of the tar shows a high concentration of lactone groups, indicated by the C=O absorption at 1773 $cm.^{-1}$ The complete disappearance of anhydride groups from the tar suggests that anhydride groups are the breaking sites and they decompose quantitatively.

The tar shows the presence of α,β–unsaturated ketone, identified by the C=O absorption at 1703 $cm.^{-1}$ The IR spectrum also shows a relatively small aromatic and aliphatic content. Weak absorptions at 1604 and 3030 cm^{-1} suggests some isolated aromatic rings are present. A small absorption band at 1640 cm^{-1} corresponding to the unsaturation is also seen. Overall the tar formation takes place in a relatively early stage of scission at around 350°C.

Table 6.7. Assignment of the major peaks in the IR spectrum of the undegraded VA—MAA copolymer.

Band (cm^{-1})	Assignment
3450	(ν OH) free water molecules
3245	OH symmetric stretch
2980	CH_3 asymmetric stretch
2930	CH_2 asymmetric stretch
2870	CH_3 symmetric stretch
1700	C=O symmetric stretch
1740	C=O (ester groups)
1460	CH_2 bending deformation
1435	CH_3 asymmetric bending
1375	CH_3 symmetric bending
1248	(C—O—C) symmetric stretching
1130	(C—O—C) symmetric stretching
1025	(CH—O) symmetric stretching
950	(C—CH_3) rocking
800, 605	(O—CO) bending and other deformations (74)

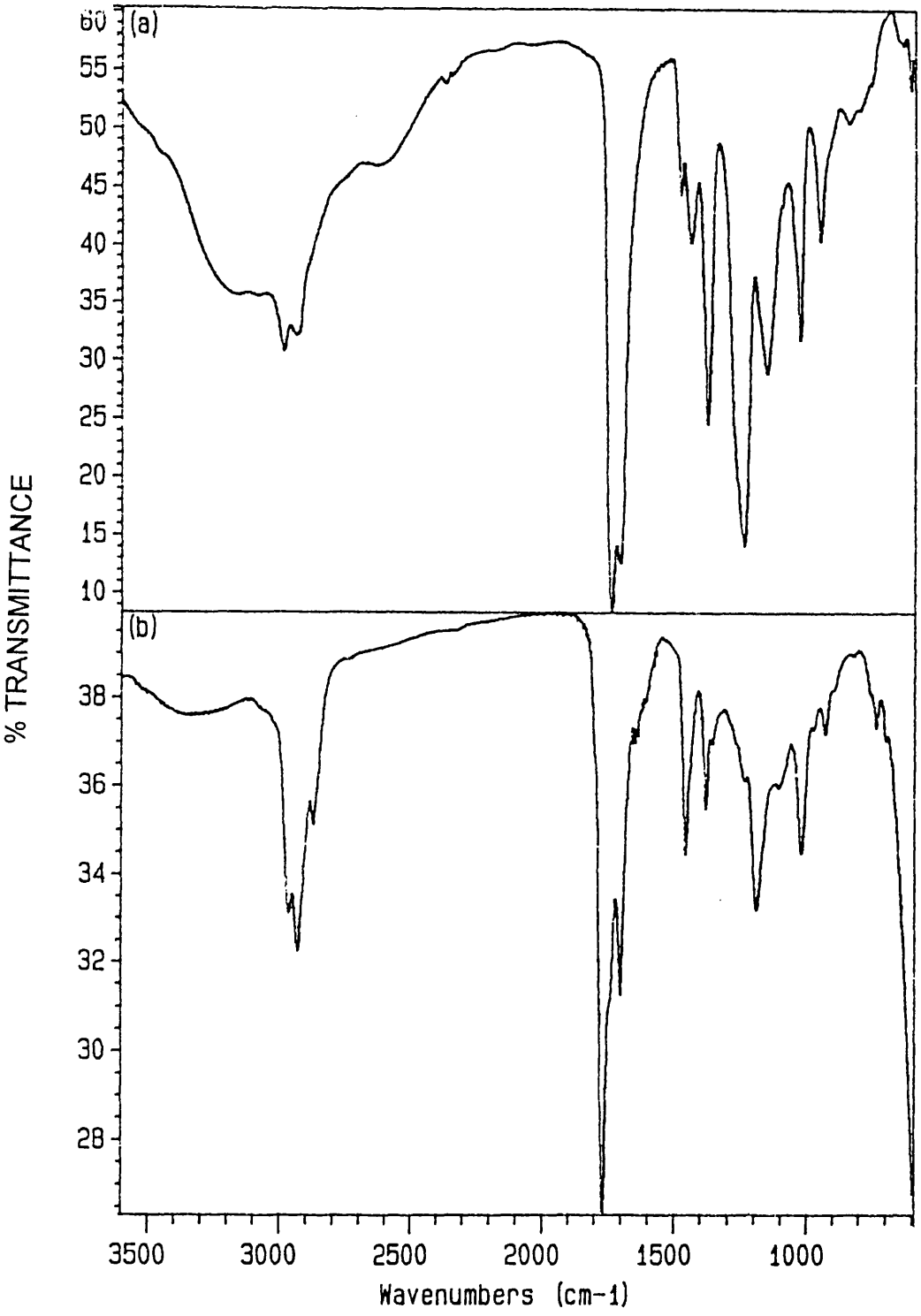


Fig. 6.7 IR spectra of (a) undegraded copolymer (b) cold ring fraction of VA—MAA copolymer degraded to 500°C under TVA conditions.

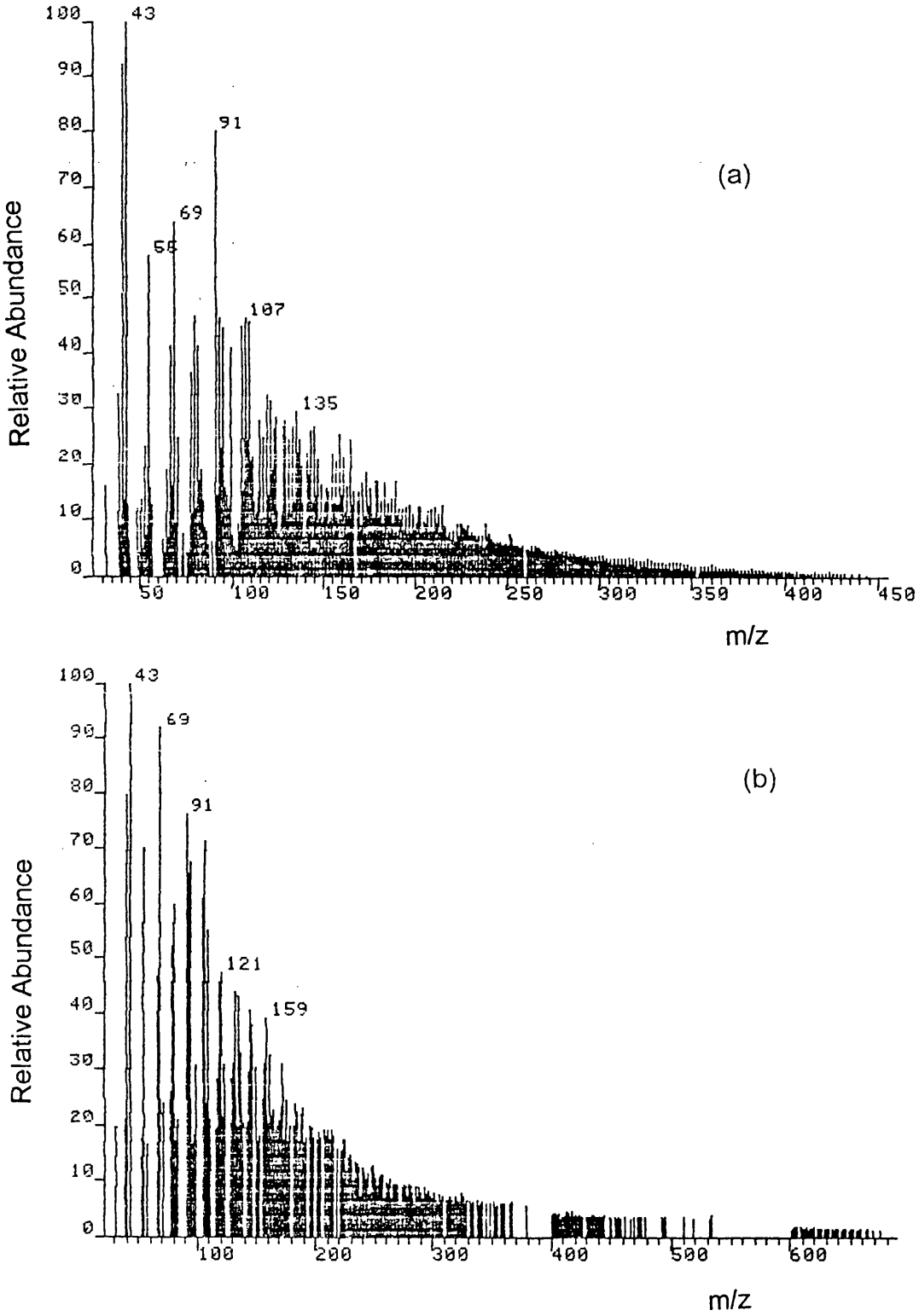
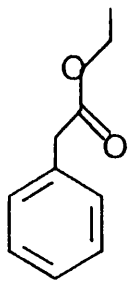
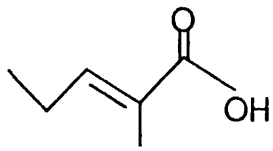
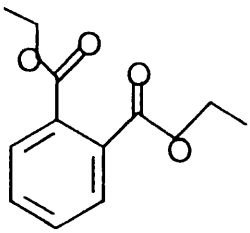
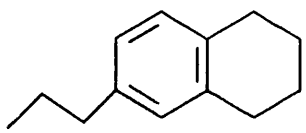
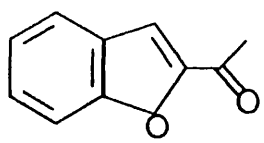
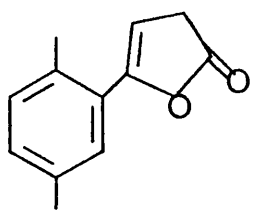
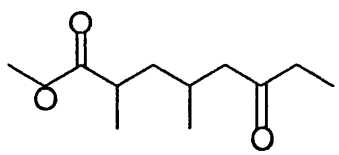


Fig. 6.8 Mass spectra of cold ring fraction (CRF) from the degradation of VA—MAA copolymer to 500°C under TVA conditions using probe temperatures of (a) 160°C (b) 220°C.

Table 6.8 The composition of the cold ring fraction (CRF) collected during the pyrolysis of VA—MAA copolymer. The products are listed according to their relative abundance

	Compound	MW
1		164
2		114
3		222
4		174
5		160
6		188
7		202

Since the anhydride rings are quite spaced, the fragments resulting through their breakdown are quite large and of reduced volatility.

At higher temperatures, the lactone rings decompose as well, increasing the frequency of scissions that produce the smaller compounds that constitute the liquid and gas fractions.

The mass spectra of cold ring fraction obtained using a probe heated to 160 and 220°C are presented in Fig. 6.8(a-b). The products identified by the GC-MS technique are listed according to their relative abundance in Table 6.8.

STUDY OF THE STRUCTURAL CHANGES IN THE COPOLYMER DURING DEGRADATION

The structural changes in the VA—MAA copolymer during thermal degradation have been investigated by FTIR reflection absorption spectroscopy using a film cast on stainless steel plate.

Typically, in a temperature-programmed experiment the changes in the copolymer structure were followed by heating a polymer film at a rate of 10°C/min to different temperature up to point of char. The heated film was then cooled rapidly with fan assistance at a rate of approximately 50°C/min.

The effect of the structural transformations upon heating the copolymer to temperatures from 200 to 500°C on the IR spectrum are illustrated in Fig. 6.9(b-h). The main absorption bands of the undegraded copolymer spectrum (Fig. 6.9a) are presented in Table 6.5.

Upon heating polymer up to 200°C, anhydride peaks appear at 1805 and 1750 cm^{-1} (Fig. 6.10b). At 280°C (Fig. 6.9c) the lactone can be identified by its peak at 1200 $cm.^{-1}$ The COOH groups have almost disappeared due to anhydride and lactone formation. The PVA sequences have lost acetate groups, as shown by the fact that the $\nu_a CH_3$ frequency has moved from 2986 cm^{-1} characteristic of CH_3-O to 2975 cm^{-1} characteristic of CH_3-C and by the fact that the 1440 cm^{-1} band (δ CH_3) is diminished compared to the 1460 cm^{-1} band (δ CH_2). It can also be noted that there is an appearance of unsaturation at a frequency typical for deacelytated VA units (1657 cm^{-1}).

The polymer heated up to 320-360°C shows massive decomposition of anhydride rings Fig. 6.9(d&e). Towards 360°C, lactone begins to decompose as well.

The spectrum of copolymer heated up to 400°C (Fig. 6.9f) shows that ester groups have disappeared completely. The anhydride groups have extensively decomposed, but some lactone groups have survived. Some aromatic structures are apparently present, but without the bands in the 3100-3000 cm^{-1} and 1600-1500 cm^{-1} regions, the latter always present with condensed rings. The other significant change in the spectrum is the appearance of α,β–unsaturated ketone indicated by the carbonyl absorption at 1703 $cm.^{-1}$ These α,β–unsaturated ketones are probably formed on an aliphatic hydrocarbon chain. The peak at 1375 cm^{-1} is split, with a component at 1355 $cm,^{-1}$ which is probably due to end chain branches resulting from a scission process. End-chain branching has not been observed with PMAA, but it is known to result from the decomposition of lactone groups (82).

At 440°C (Fig. 6.9g) the char of the copolymer is intermediate between those of the corresponding homopolymers, but has no one more element.

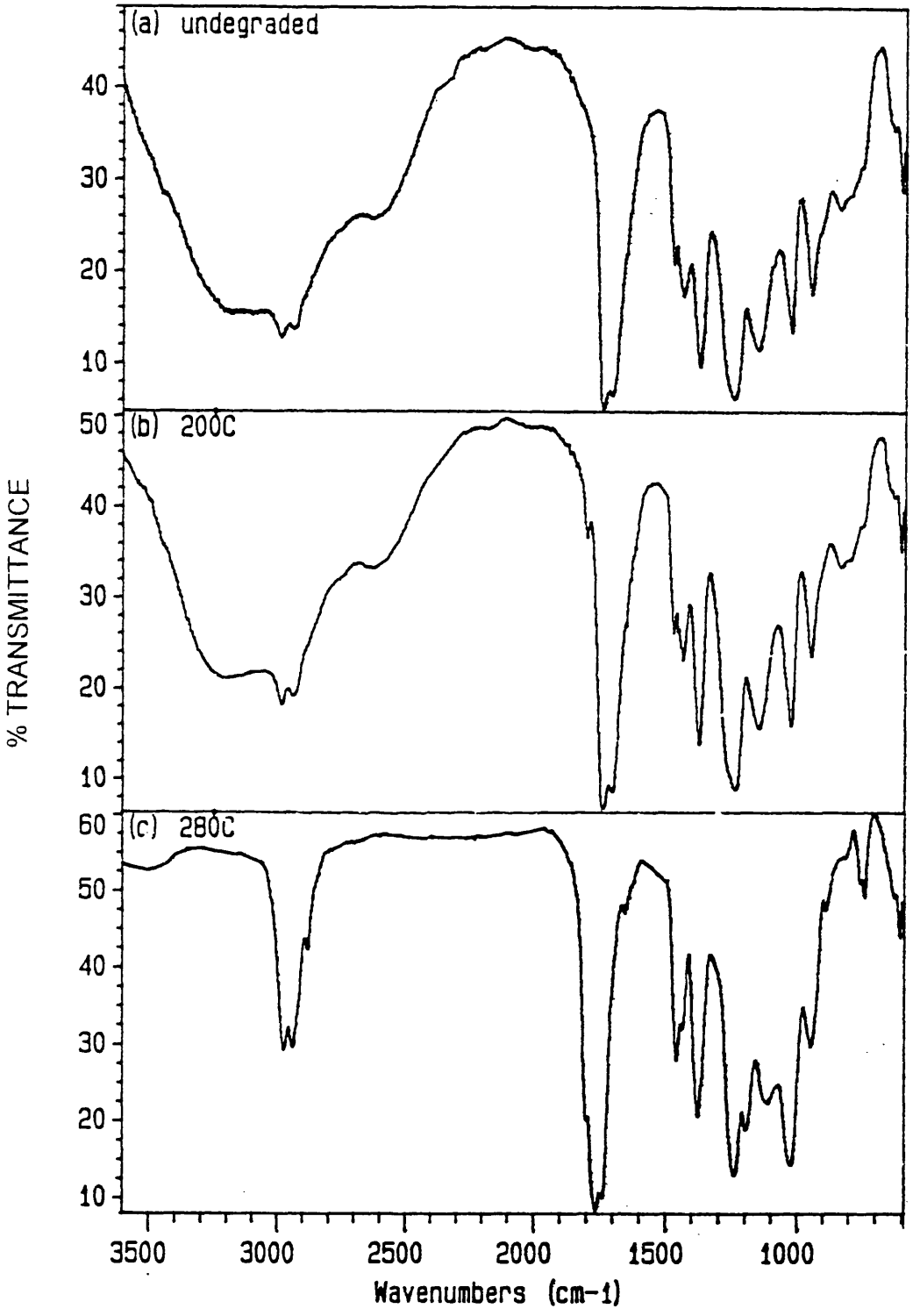


Fig. 6.9 Infrared spectra of VA—MAA copolymer: (a) before and after heating in vacuum to: (b) 200°C (c) 280°C.

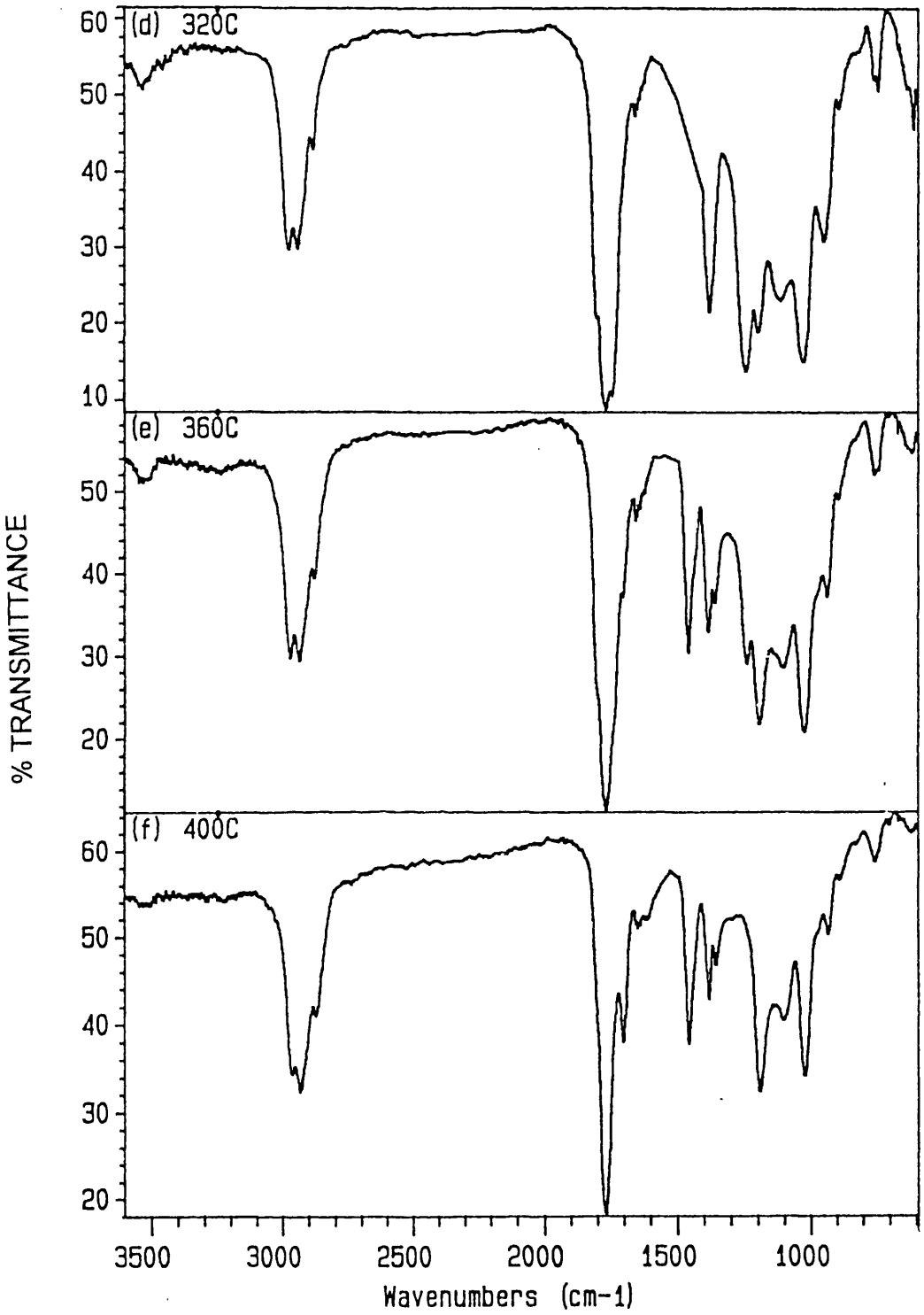


Fig. 6.9 Continued (d) 320°C (e) 360°C (f) 400°C.

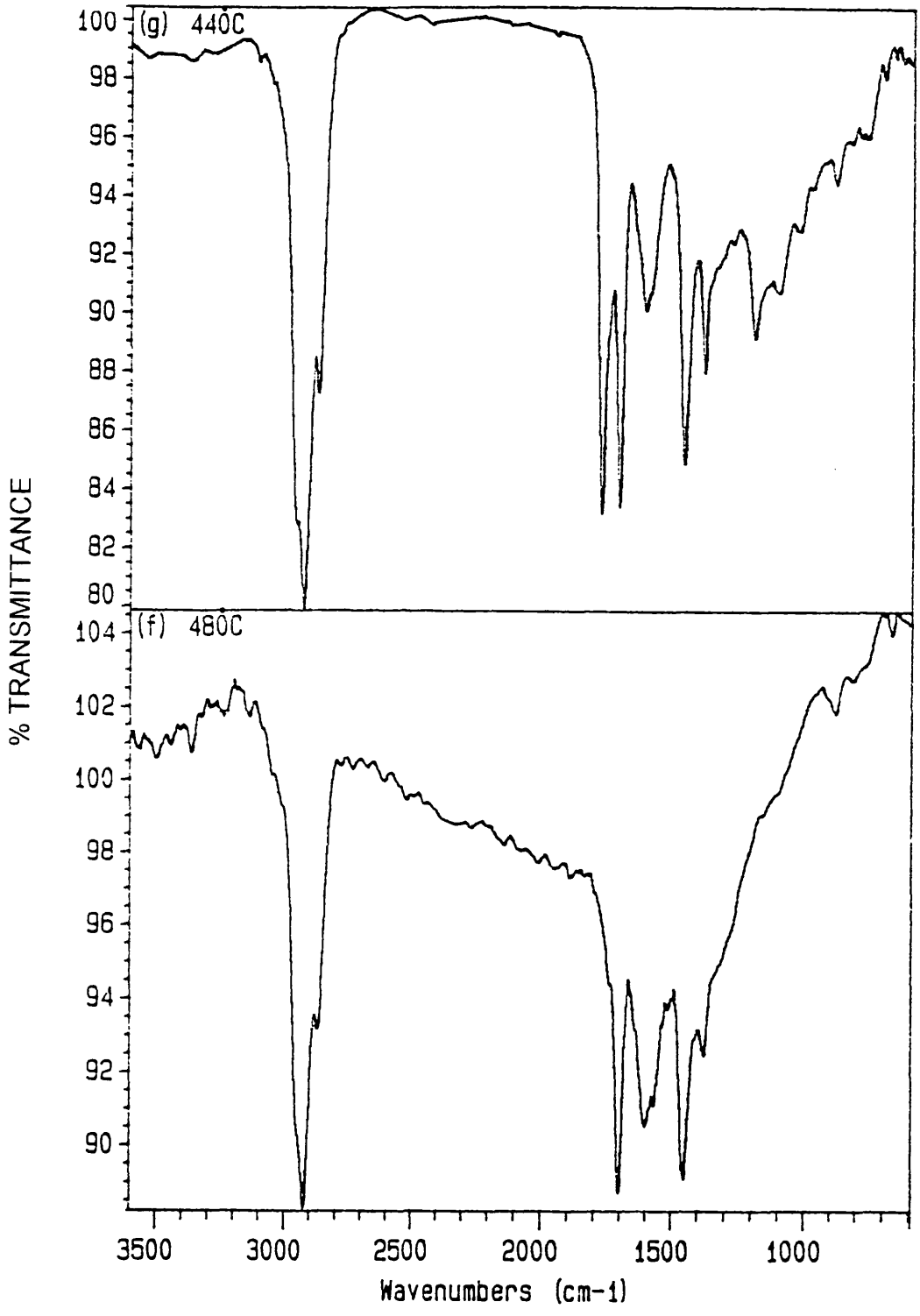


Fig. 6.9 Continued (g) 440°C (h) 480°C.

Next to the aromatic rings (quite substituted) and to the remaining hydrocarbons, there is an important concentration of lactone ring and an increased concentration of α,β–unsaturated ketone groups.

The lactone groups are lost at 480°C (Fig. 6.9h) and the structure of the char more closely resembles that from PMAA with pentasubstituted aromatic rings (only isolated H atom vibrations at 880 cm^{-1} are present) and CH_3 branches. It seems that the lactone rings which prevented the condensation of aromatic rings decompose thereby enabling polycondensation to proceed.

ISOTHERMAL DEGRADATION AT LOWER TEMPERATURE

The VA—MAA copolymer was also degraded isothermally at lower temperature to study further the initial stages of degradation. The film was cast on a stainless steel plate and dried using the same method as described previously. The supported film was heated at 170°C for various lengths of time, cooled down to room temperature and the spectroscopic changes in the IR spectrum at different times of heating were recorded.

The spectrum of undegraded copolymer is presented in Fig. 6.10a, in which the main peaks of PVA and PMAA can be recognised. Isothermal heating of the copolymer at 170°C for various time intervals (Fig. 6.10b-d) allows one to detect the transformations of the VA and MAA sequences alone and the reactions between neighbouring VA and MAA units. Heating for 20 min at 170°C leads to the formation of the anhydride rings in the MAA sequences which can be observed by the newly appeared peaks at 1804, 1750 and 1025 $cm.^{-1}$

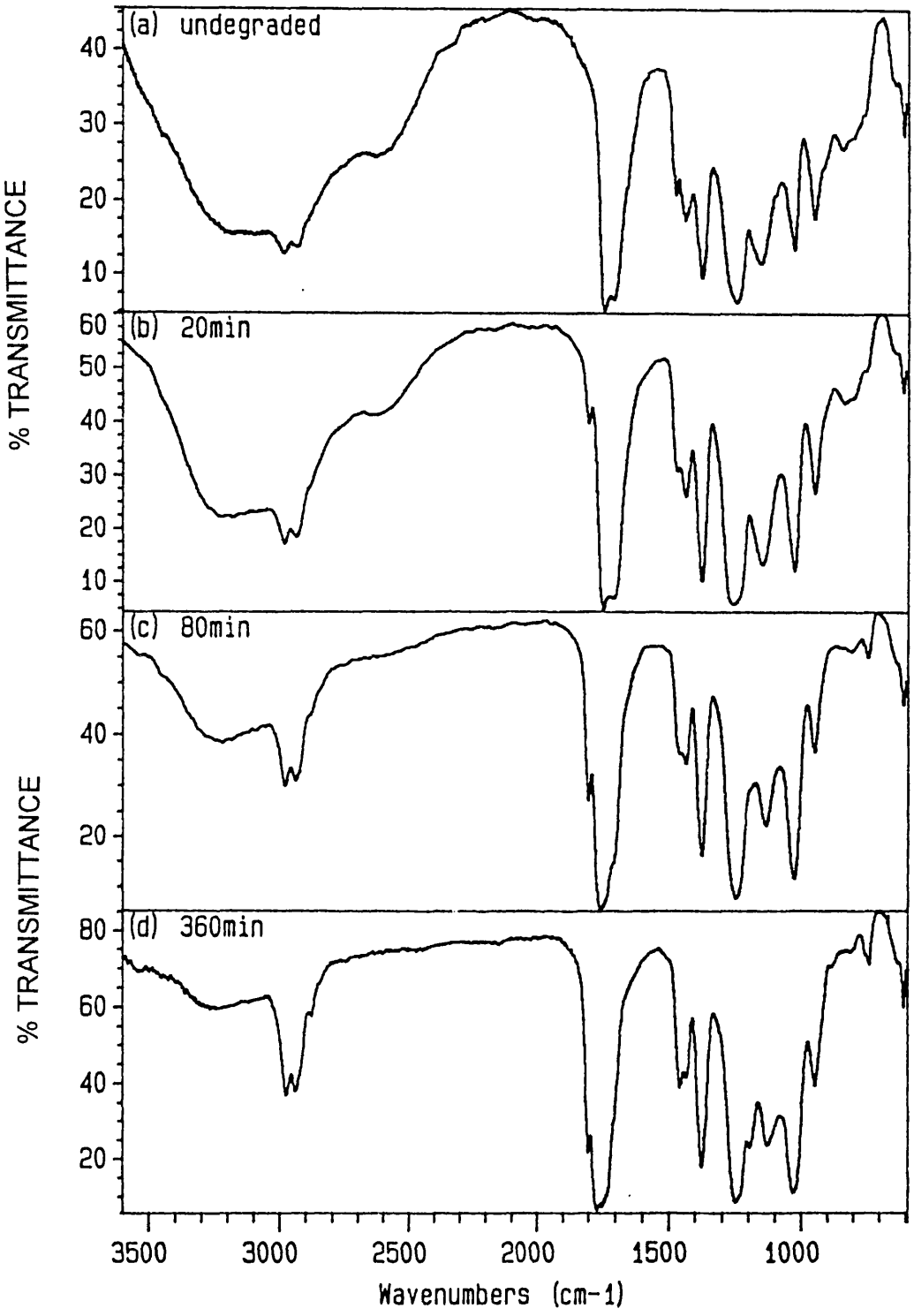


Fig. 6.10 Infrared spectra of the VA-MAA copolymer: (a) before and (b) - (d) after heating in vacuum for various times.

Heating for 80 min at 170°C leads to more advanced anhydride formation (Fig. 6.10c) and further increase of the corresponding peaks, while the peaks of the acidic dimer (1705, 1150, 950 cm^{-1}) decrease.

Heating at 170°C for 6 hrs (Fig. 6.10d) strongly decreases the peaks of the acidic dimer (3250, 1705, 1150, 950 cm^{-1}) which is transformed into anhydride. A new species, with peaks at 1775 and 1203 cm^{-1}, is lactone formed at the interface of the VA and MAA sequences. Lactone formation has also been observed in the thermal degradation of the crotonic acid—vinyl acetate alternating copolymer (82) which eliminate acetic acid; in vinyl acetate- methyl methacrylate copolymers (68) which eliminate methyl acetate and in vinyl chloride—methyl methacrylate copolymers which eliminate methyl chloride (83) to form the lactone.

DISCUSSION

The VA—MAA copolymer presents three degradation stages, which partly overlap. During the first stage, between 200 and 300°C the anhydrisation of some of the COOH groups takes place through the elimination of water molecules. IR spectra show that towards 280°C lactone units form between alternating VA and MAA units with the elimination of acetic acid and that unsaturation does not develop until 280°C. The VA units which deacetylated in PVA at 160°C seem to be more stable in the VA—MAA copolymer when they are present as short, isolated sequences. This is consistent with the hypotheses of "chain" deacetylation in PVA.

In the second stage of degradation between 280 and 350°C, lactone continues to form, but anhydride begins to decompose. Although steric effects on anhydride and lactone formation have not been examined, it is

likely that lactone formation puts an additional strain on the macromolecular chain, which is already strained by the formation of rigid anhydride groups containing two quaternary C atoms (see anhydride structure in Scheme 2 Chapter 5).

The copolymer degraded above 280°C consists of lactone rings separated by short sequences of double bonds, demonstrating that lactone groups are considerably more stable than anhydride groups. As in PMAA, the formation of the aromatic rings cannot be clearly ascertained in the VA—MAA copolymer until 400°C.

Anhydride structures completely disappear by 400°C, while the lactone rings remain in the charred polymer up to 480°C which shows that they are a more thermally resistant species. Anhydride decomposition in the VA—MAA copolymer takes place much earlier than in PMAA, where it occurs between 350 and 440°C. So anhydride decomposition accelerates the decomposition of the lactone groups. As a result, the polymer continuously loses weight and decomposes almost by 425°C, however, some lactones survive up to 480°C. In the third stage of degradation between 350 and 425°C mass decomposition of the anhydride and lactone rings takes place.

The VA—MAA copolymer yields a high fraction of tar (42 %). The tar contains a significant concentration of lactone groups, but no anhydride groups, proving thereby that anhydride groups are the breakdown sites and that they decompose quantitatively. The tar also shows the presence of α,β-unsaturated ketone, isolated aromatic rings with the remainder of the structure being aliphatic. Tar formation takes place in a relatively early stage of scission (around 350°C) since the anhydride rings are quite spaced and the fragments resulting through their breakdown are quite large and of reduced volatility. At higher temperatures, the lactone rings decompose as

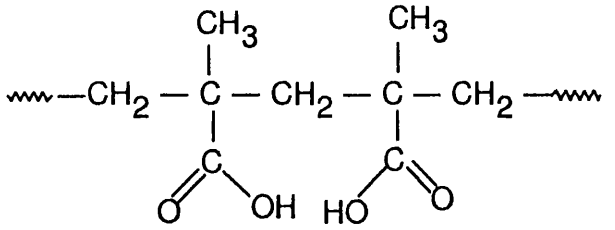
well, increasing the frequency of scission acts so that smaller products constituting the liquid and gas fraction are formed.

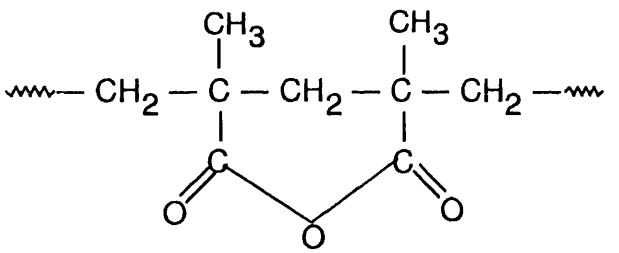
The pyrolysis of VA—MAA copolymer leads to a large liquid fraction (48%) in which the main component is the acetic acid. Together with water it accounts for 81-90% of the liquid fraction (Table 6.4). The acetic acid and water content are only rough estimates since exact measurements were not carried out. The large cold ring fraction (42%) is characteristic for the decomposition of the anhydride groups and a high yield was recorded for PMAA degradation as well. PVA produces less cold ring fraction (19%). Table 6.5 gives the detailed composition of the liquid fraction after the removal of the water and acetic acid. In general, the proportions of the classes of products obtained in the pyrolysis of VA—MAA copolymer tend to be intermediate between those from tar PVA and PMAA. On a qualitative level, the aromatic hydrocarbons present in the liquid fraction from the VA-MAA copolymer have a lower degree of substitution compared with PMAA. Trimethylbenzene which forms in PMAA pyrolysis in high concentration (25%) is only present in small concentration (3.5%) among the degradation products of the copolymer which is consistent with the facts that (i) the copolymer has a high proportion of alternating units and short sequences of methacrylic acid and (ii) many of the of methacrylic acid units take part in lactone, rather than anhydride formation.

Scheme 1 explains the formation of anhydride rings between adjacent MAA units and, concurrently, lactone units through the elimination of acetic acid between adjacent acid and ester groups. The degradation mechanism of the anhydride ring has been discussed in detail in Chapter 5.

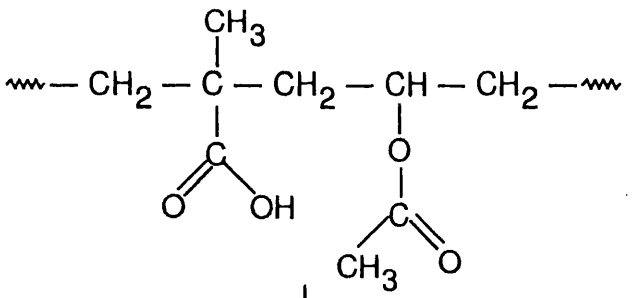
Mechanism for thermal degradation of VA—MAA copolymer

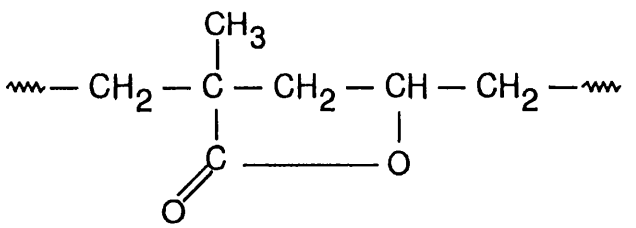
Scheme 1





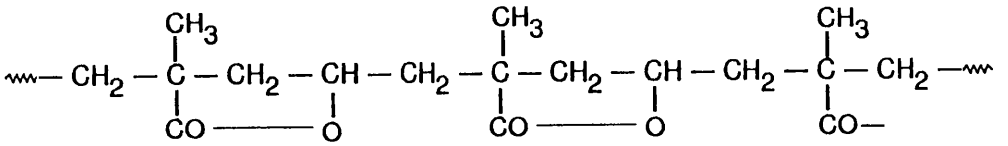
+ H_2O (1)

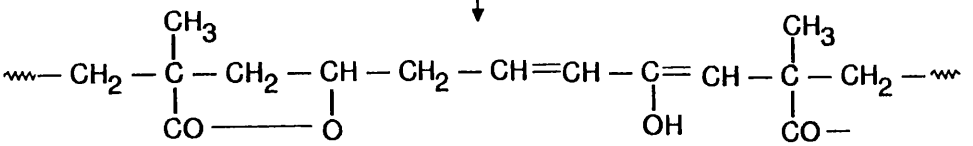




+ CH_3COOH (2)

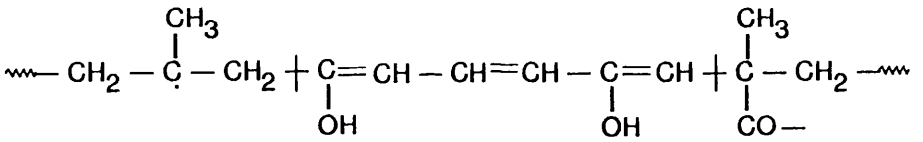
Scheme 2





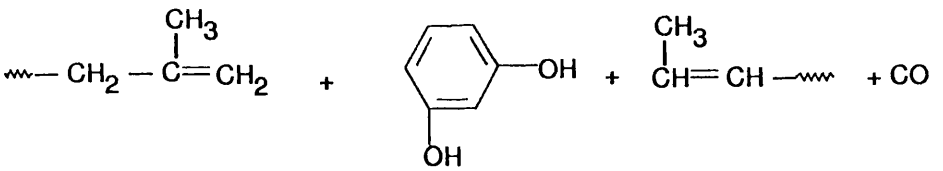
(1)

+ CO + CH_4



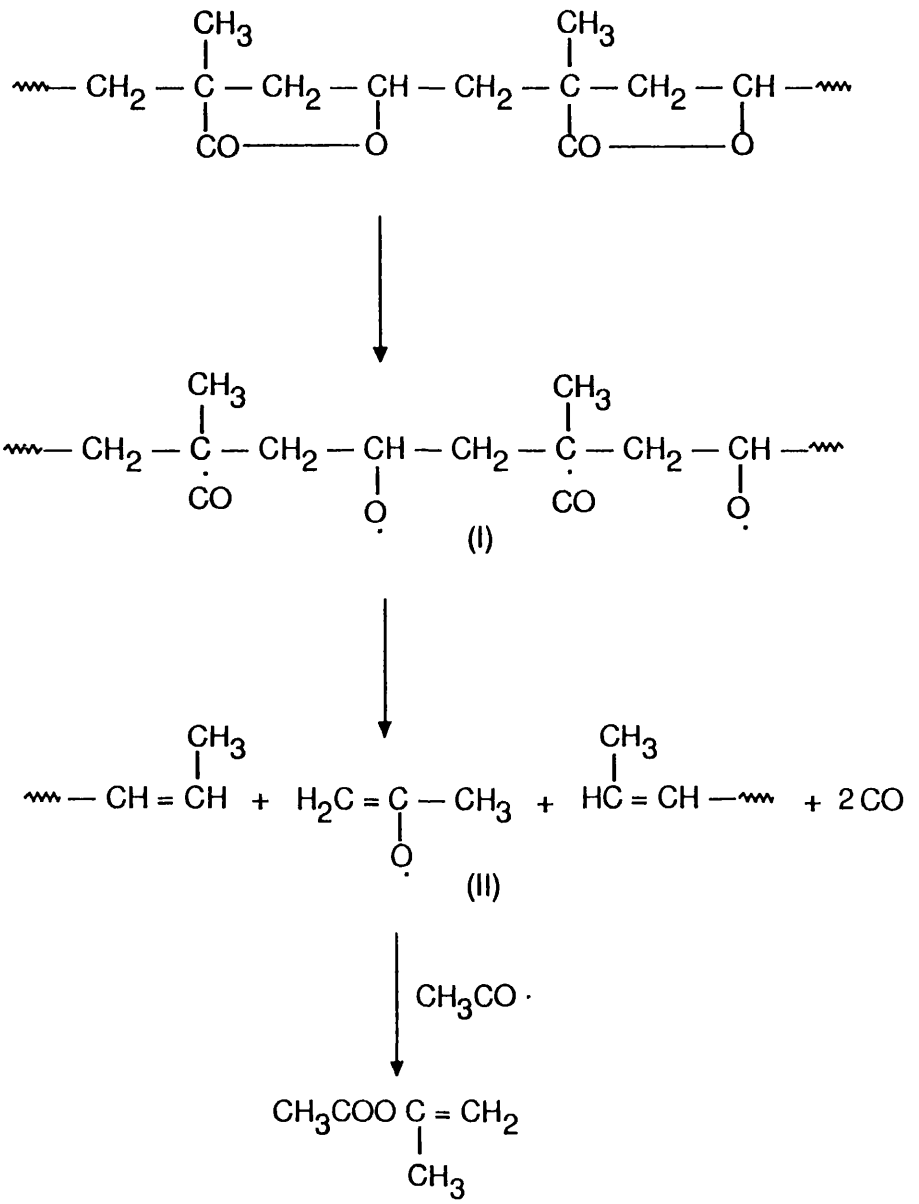
(2)

+ CO + H



(3)

Scheme 2 (continued)



(I)

(II)

(5)

The most important O-containing compound in Table 6.5 is resorcinol (no. 26). Its formation can only be explained through the decomposition of the lactone (reactions 3-4, Scheme 2) as PVA does not form resorcinol and produces a very small fraction of O-containing products.

An interesting product is acetic acid, 2-propenyl ester (no. 24, Table 6.5). It is clear that it can only appear through the recombination of propenoxy and acetyl radicals as it is not possible to break C—C bonds on the macromolecular chain while preserving ester bonds attached to it. It is obvious from its structure that this compound can only be formed through the decomposition of the lactone. Reaction (5), Scheme 2 features such a process. Reaction 5 does not necessarily mean that scission is followed by recombination. They may well be simultaneous.

The other O-containing products in Table 6.5 can be formed through the decomposition of anhydride, as well as lactone groups, judging from their structure. However, the decomposition products of the lactone group (resorcinol and acetic acid, 2-propenyl ester) prevail in the liquid fraction.

CONCLUSION

The VA—MAA copolymer degrades in three stages. Anhydride formation (intramolecular) between 200 and 300°C, is accompanied towards the end of the stage by lactone formation between adjacent VA and MAA units. As lactone continues to form in the second stage (280-350°C), anhydride groups begin to decompose prematurely. The anhydride decomposition is due to the strain put on the macromolecular chain by lactone formation. The result is an accelerated decomposition of the copolymer over the temperature interval between 350 and 425°C, which constitutes the third stage of decomposition. The polymer forms a high tar fraction (42%)

containing lactone groups, but no anhydride groups, showing that the anhydride groups decompose first. It seems that most of the anhydride groups decomposes in the process of tar formation. Indeed, the major products in the liquid fraction have structures that can only be explained through lactone decomposition.

As a general conclusion, the studied copolymer and the corresponding homopolymers, which are discussed in previous chapters, present different degradation patterns. PVA has a strong tendency towards crosslinking and aromatic ring formation which is overcome at higher temperatures by the scission of the aliphatic parts. PMAA forms an extensive system of anhydride links which protects it against further degradation up to 350°C. Above this temperature, the resulting poly(anhydromethacrylic acid) breaks down with massive scission. In the VA—MAA copolymer both crosslinking mechanisms are perturbed due to the reduced, length of the sequences of either monomer. The copolymer forms anhydride rings in the MAA sequences and a large proportion of lactone rings between alternating MAA and VA units. Lactone formation induces early decomposition of the whole polymer. The VA—MAA copolymer is thermally less stable than the corresponding homopolymers i.e. PVA and PMAA.

CHAPTER SEVEN

THERMAL DEGRADATION STUDIES OF THE ALTERNATING COPOLYMER OF VINYL ACETATE AND CROTONIC ACID

INTRODUCTION

The thermal decomposition of random copolymers of vinyl acetate with monomers such as methyl methacrylate, styrene, ethylene, (68) vinyl chloride (84,85), has been studied in detail whilst that of alternating copolymers remain largely unexplored.

Because of the strictly ordered sequence of monomer units alternating copolymers can show interesting behaviour during degradation. For example, in the vinyl acetate—maleic anhydride system (33), the vinyl acetate units undergo side group scission before extensive backbone scission occurs. Similarly in the acenaphthylene—maleic anhydride copolymer (86) the maleic anhydride units decompose initially. By controlled degradation of these copolymers novel polymer structures can be formed. In other cases chemical interaction between the two types of monomer unit can be envisaged as the temperature is raised.

In this chapter the thermal degradation of the alternating copolymer of vinyl acetate (VA) with crotonic acid (CA) has been examined.

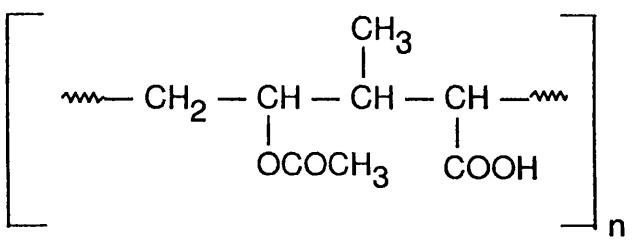


Table 7.1 The preparation conditions for the vinyl acetate—crotonic acid alternating copolymer made by free radical polymerisation.

Amount of crotonic acid	33.6 g
Amount of vinyl acetate	8.4 g
Amount of initiator (AIBN)	0.2 %*
Time of polymerisation	6 hours
Temperature of polymerisation	68°C
Conversion	5.8 %

* Relative to the total weight of monomers

The VA—CA alternating copolymer was synthesised by free radical polymerisation using AIBN an initiator. The purification of monomers and the polymerisation methods are described in Chapter 3, while the preparation conditions are listed in Table 7.1.

Thermal degradation studies have been carried out under programmed heating up to 500°C in nitrogen and vacuum conditions using DSC, TG and TVA. The various fractions from TVA (cold ring, liquid fraction, residue) were collected and weighed for material balance after pyrolysis. In addition, IR spectroscopy has been used to determine the structural changes in the copolymer under ramped and isothermal heating conditions.

THERMOGRAVIMETRY (TG)

The thermogravimetric (TG) and differential thermogravimetric (DTG) curves for VA—CA copolymer were obtained under dynamic nitrogen at a heating rate of 10°C/min up to 500°C.

The TG curve presented in Fig. 7.1 shows that VA—CA copolymer decomposes in two main stages. The DTG curve shows an initial peak from ambient temperature to about 120°C, which is due to solvent and moisture from the sample.

A weight loss of 33% is observed in the temperature region 200-310°C. In this temperature region there are, in fact, two stages of degradation, the first one of very small magnitude between 200 and 240°C which is followed by the main stage between 240 and 310°C.

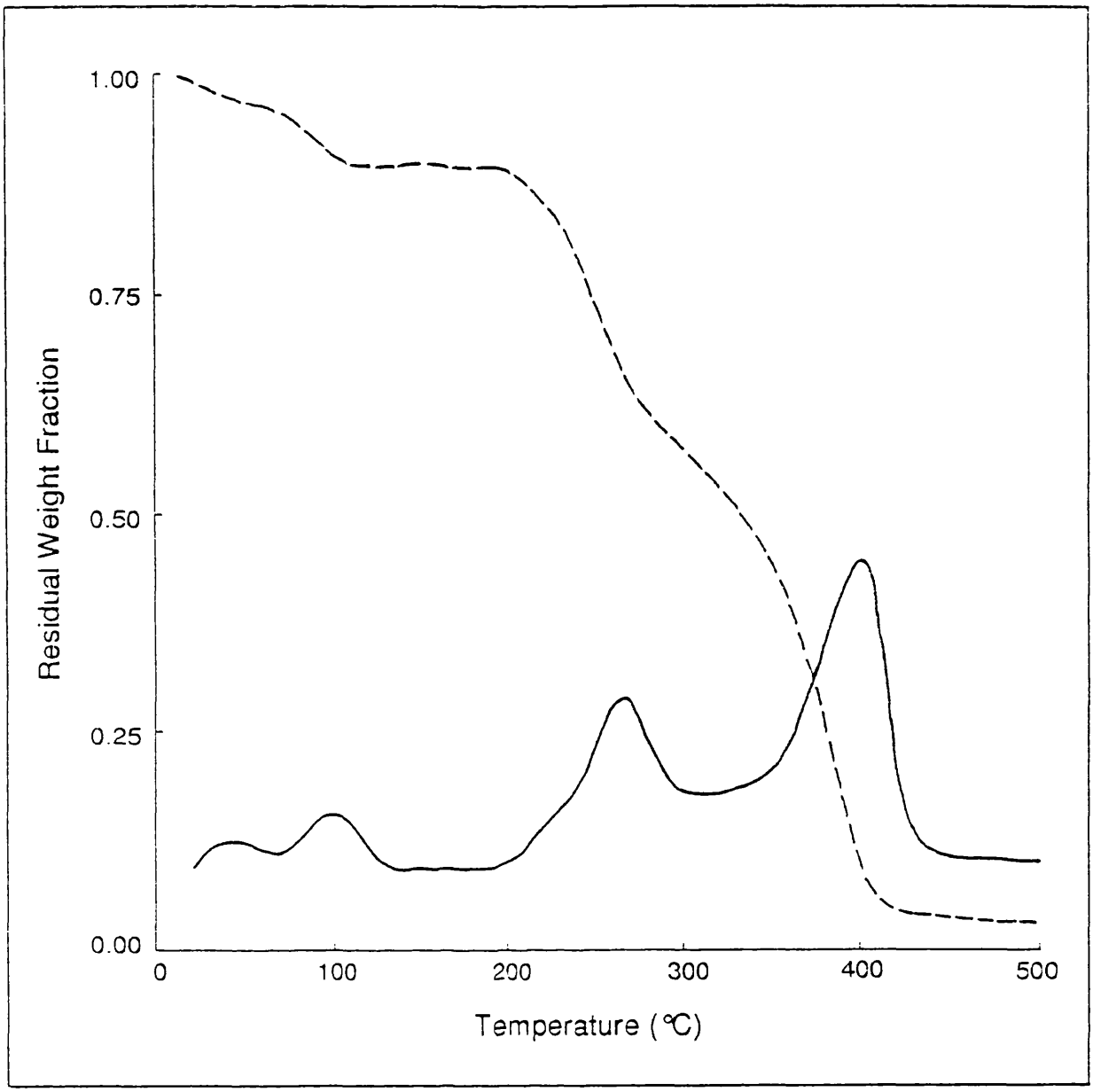


Fig. 7.1 TG and DTG curves for VA—CA copolymer (heating rate 10°C/min, nitrogen flow)

The second and main stage of degradation is between 320 and 450°C with a rate maximum around at 400°C. A weight loss of 60% is observed in this stage. At 500°C the TG curve indicates very little residue remains (3.5%).

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The thermal stability of the VA—CA copolymer was also studied by DSC. A sample of approximately 5mg in powder form was heated up to 500°C at 10°C/min under a nitrogen flow of 70ml/min. The result obtained for the copolymer is shown in Fig. 7.2 with the features listed in Table 7.3.

The DSC curve shows two main endotherms. The first one, between 200 and 300°C with a thermal effect of 81.5 J/g, corresponds to the weight loss of 33% observed in the first stage of decomposition indicated in the TG curve. It is interesting to note that there is a small shoulder at 240°C which was also observed in the TG curve (Fig. 7.1).

The DSC curve shows a very shallow endotherm between 310 and 350°C with a thermal effect of only 8J/g. A major DSC endotherm appears between 350 and 450°C and corresponds to the second stage of degradation in the TG curve. The enthalpy associated with this endotherm is 148J/g.

THERMAL VOLATILISATION ANALYSIS (TVA)

The thermal degradation was conducted under vacuum up to 500°C at a heating rate of 10°C/min. The evolution of products was followed by thermal volatilisation analysis (TVA). Several fractions of the evolved products were separated according to the guidelines of this technique, which have been outlined in Chapter 2.

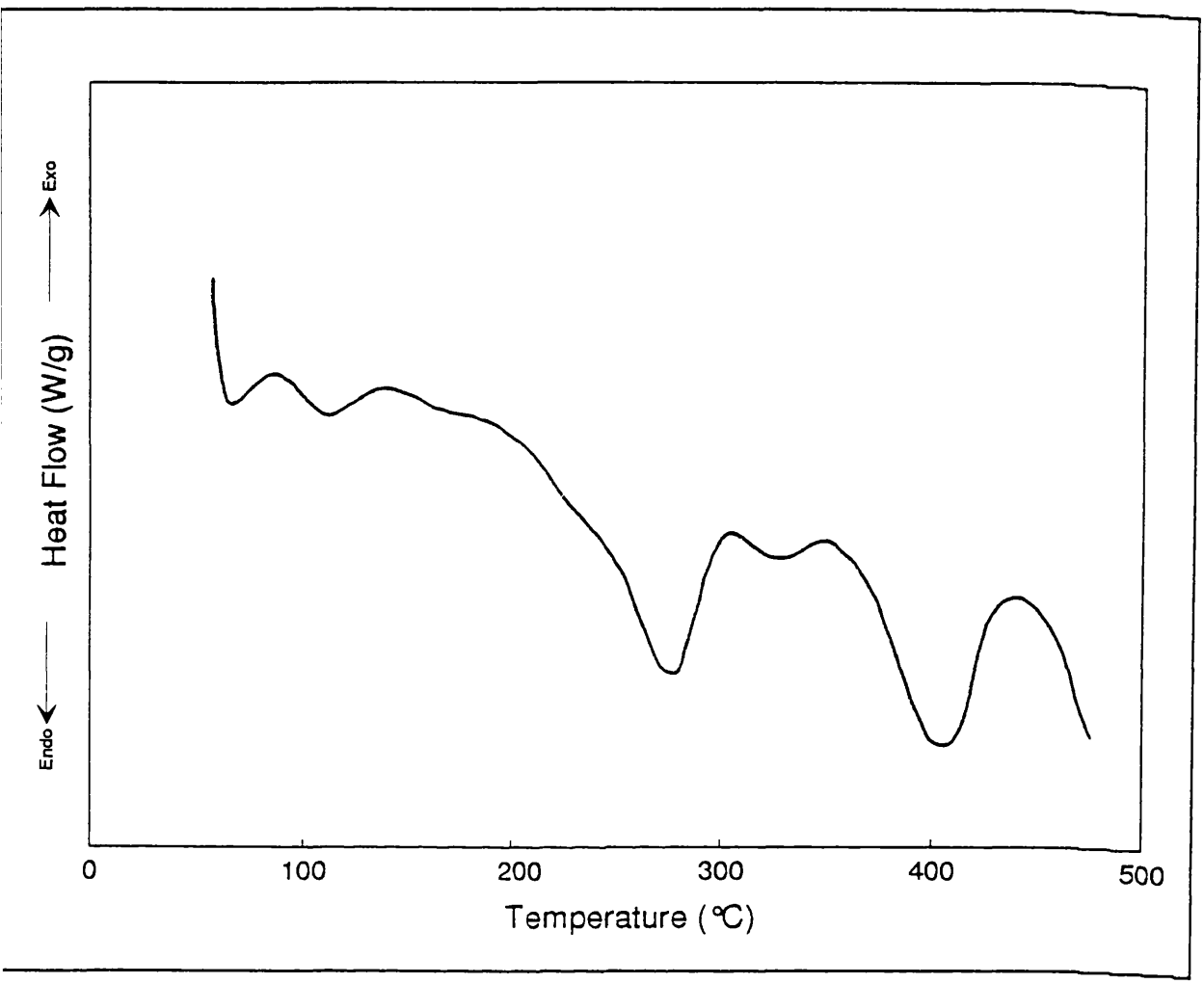


Fig. 7.2 DSC curve for VA—CA copolymer (heating rate 10°C/min under nitrogen flow).

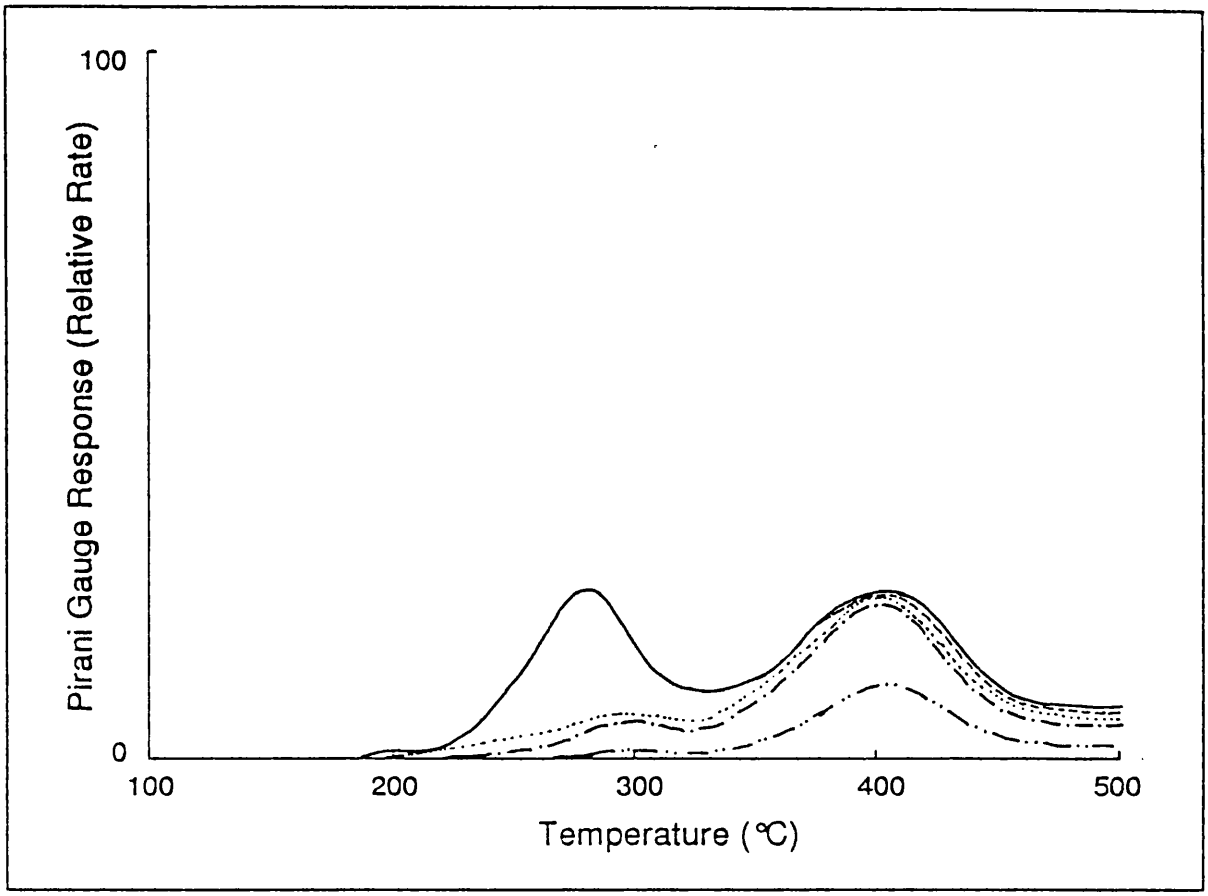
The TVA trace for the VA—CA copolymer presented in Fig. 7.3 shows the pressure readings obtained on the Pirani gauges due to the volatile products which escape the traps at -196, -100, -75,-45 and 0°C as a function of the temperature of the sample. It can be seen that the thermal decomposition

consists of two stages, in agreement with the TG and DSC results, the first one between 200 and 330°C, the second one between 330 and 460°C. The TVA curve for the copolymer has an initial small peak from 80°C to 120°C, which is due to the loss of solvent and absorbed moisture from the sample. In the first stage of degradation there is a very small fraction of non-condensable gases, consisting mainly of carbon monoxide together with some methane. This fraction is larger in the second stage of degradation.

The products at the first stage are almost entirely acetic acid (collected at trap temperatures below -45°C) together with a small amount of CO_2, volatile at -100°C but trapped at -196°C. In the second stage, the product volatility suggests this has reversed with a large fraction of CO_2 and very little acetic acid. A black carbonaceous residue was observed after the TVA experiment.

At the end of the TVA experiment, the main product fractions, collected on the basis of different volatility, were determined quantitatively by direct weighing giving the results in Table 7.2. The products consists mainly of condensable gases and liquids (43%) and cold ring fraction (47%) plus smaller fractions of residue and non-condensable gases. The non-condensable gases are calculated by difference.

The TVA, TG, DTG and DSC data for the copolymer are summarised in Table 7.3.



Key

0℃
-45℃
-75℃
-100℃
-196℃

Fig. 7.3 TVA curve for VA—CA copolymer sample heated in vacuum to 500°C at 10°C/min.

Table 7.2 The material balance of the fractions collected during the degradation to 500°C of the VA—CA copolymer in a TVA experiment

No	Fraction	%
1	Condensable gas and liquid fraction	43
2	Cold ring fraction (tar)	47
3	Residue	7.0
4	Non-condensable gases (by difference)	7.0

Table 7.3 TVA, DTG, TG and DSC data for VA—CA copolymer

TVA		DTG		TG	DSC	
Temp. range C	Peak temp. °C	Temp. range °C	Peak	% weight loss for stages	Temp. range °C	Peak temp. °C
200-320	265	200-310	268	33	200-320	270
330-460	400	330-460	400	52	350-450	405

IDENTIFICATION OF DEGRADATION PRODUCTS

SUBAMBIENT THERMAL VOLATILISATION ANALYSIS (SATVA)

The condensable gases and liquids collected during the degradation of the polymer in the TVA system were separated into their components by the SATVA method. Mass spectroscopic analysis was carried by bleeding the products, as they evolved from the cold trap, into the mass spectrometer coupled to the TVA system. The condensable gases were collected and examined by IR spectroscopy.

The SATVA curve presented in Fig. 7.4 shows five peaks. The fraction corresponding to shoulder 1 consisted of hydrocarbons such as ethene, propene and n-hexane (this was used as precipitant). The peak 2 fraction consisted entirely of CO_2. At peaks 3 ,4 and 5 acetic acid is predominant, obscuring the other components, although some ketene could be identified at peak 3. For this reason an experiment was conducted in which the compounds evolved during each stage of degradation, i.e. at the two peaks of Fig. 7.3, were collected and analysed separately.

In the liquid fraction for peak 1 (Fig. 7.3), only acetic acid could be identified. While acetic acid was still evolved in the second stage of degradation and collected at the second peak, its concentration was not overwhelming and other compounds could be identified by GC-MS.

The liquid fraction for peak 2, corresponding to the second stage of degradation (330-500°C), has also been examined by GC-MS. The products are listed in Table 7.4 according to their relative abundance.

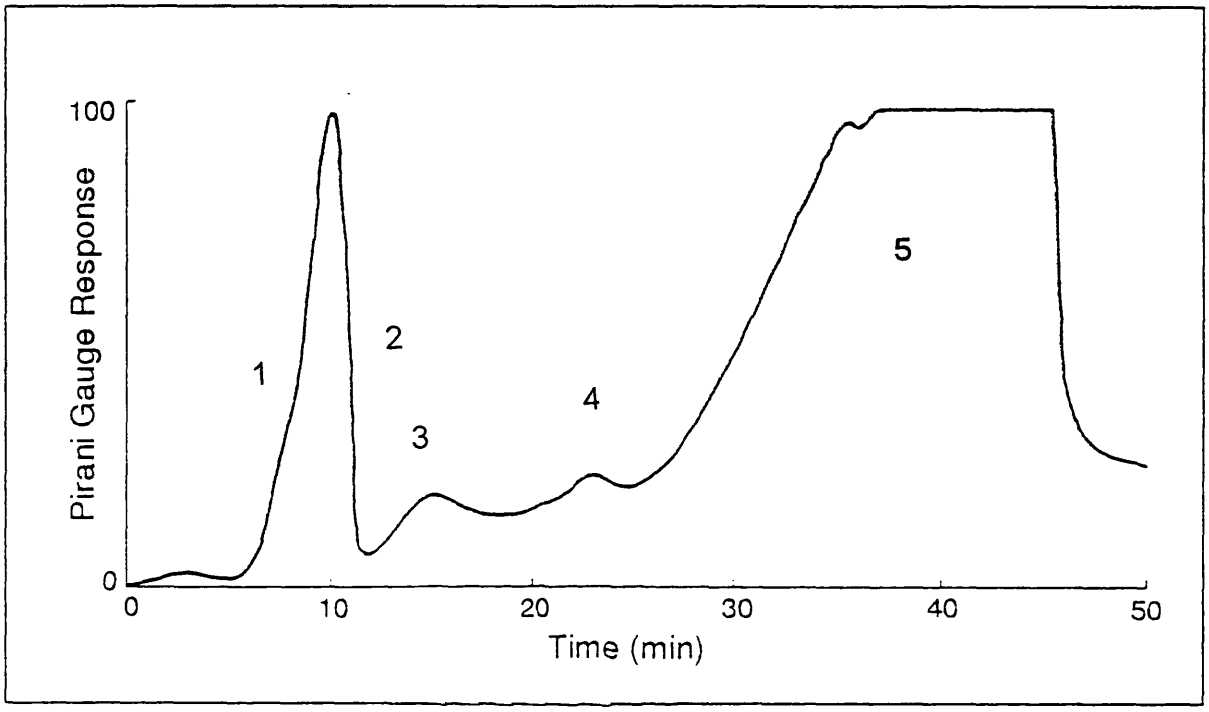


Fig. 7.4 SATVA curve for separation of the condensable volatile degradation products from degradation under TVA conditions to 500°C of the VA-CA copolymer.

Table 7.4 The composition of the liquid fraction collected during the pyrolysis of CA—VA copolymer

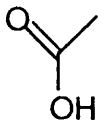
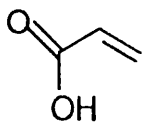
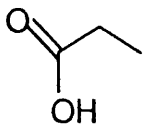
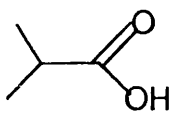
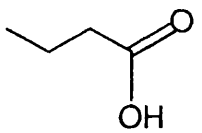
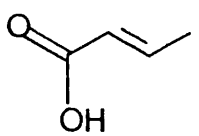
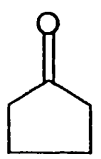
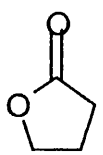
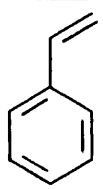
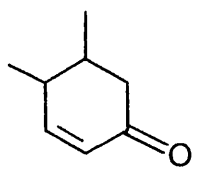
	Compound	MW
1		60
2		72
3		74
4		88
5		88
6		86
7		84
8		86
9		104
10		124

Table 7.4 Continued

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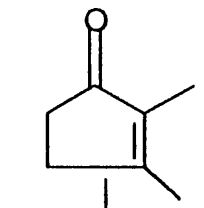
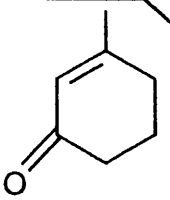
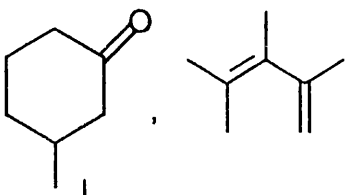
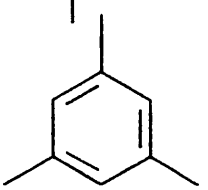
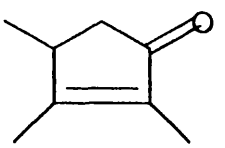
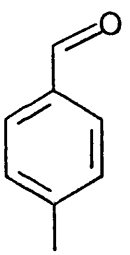
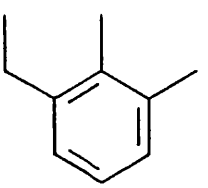
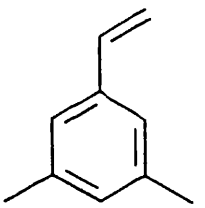
11		110
12		110
13		112
14		120
15		124
16		120
17		134
18		132

Table 7.4 Continued

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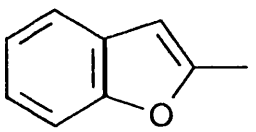
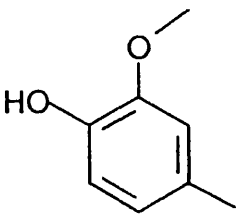
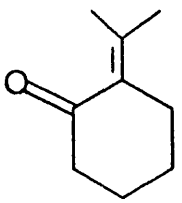
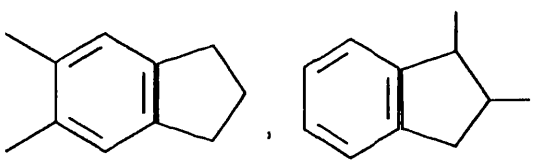
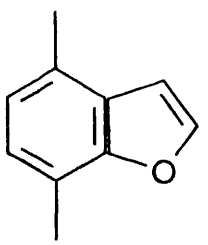
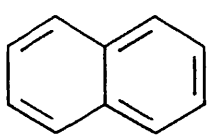
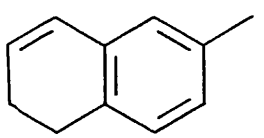
19		132
20		138
21		138
23		146
24		146
26		128
27		144

THE COLD RING FRACTION

The CRF was collected from the upper part of the TVA tube for quantitative determination by transferring it to a weighing bottle using a suitable solvent which was then evaporated. The CRF was also examined by IR spectroscopy (Fig. 7.5b), probe-MS and GC-MS.

The IR spectrum of the undegraded copolymer is also presented for comparison in Fig. 7.5a. The assignments of the main absorption peaks of undegraded VA—CA copolymer are presented in Table 7.5.

The main features of the CRF spectrum are the strong lactone absorptions present at 1770 and 1170 $cm.^{-1}$ The spectrum is similar to that of the lactonised copolymer, but the aliphatic C—H stretch bands are relatively stronger, suggesting aliphatic chain fragments containing lactone rings. The CRF spectrum also shows weak absorptions at 3080 and 1640 $cm.^{-1}$ corresponding to unsaturation

The cold ring fraction examined by mass spectrometry using a probe heated to 220 and 330°C gave the complex spectra presented in Fig. 7.6(a-b). The mass spectra indicates a mixture of materials with an m/z ratio up to approximately 400 at 220°C and 500 at 330°C.

FTIR STUDIES OF STRUCTURAL CHANGES IN THE COPOLYMER

The structural changes in the VA—CA copolymer during the thermal degradation have been investigated by FTIR reflection absorption spectroscopy using a film cast on a polished stainless steel plate.

Table 7.5. Assignment of the major peaks in the IR spectrum of the undegraded VA—CA copolymer.

Band (cm^{-1})	Assignment
2980	CH_3 asymmetric C—H stretch
2930	CH_2 asymmetric C—H stretch
2885	CH_3 symmetric C—H stretch
1740	C=O stretch of ester group
1720	C=O stretch of acid group
1460	CH_2 bending deformation
1440	CH_3 asymmetric bending
1375	CH_3 symmetric bending
1248	(C—O—C) symmetric stretching
1130	(C—O—C) symmetric stretching
1025	(CH—O) symmetric stretching
950	(C—CH_3) rocking
800, 605	(O—CO) bending and other deformations

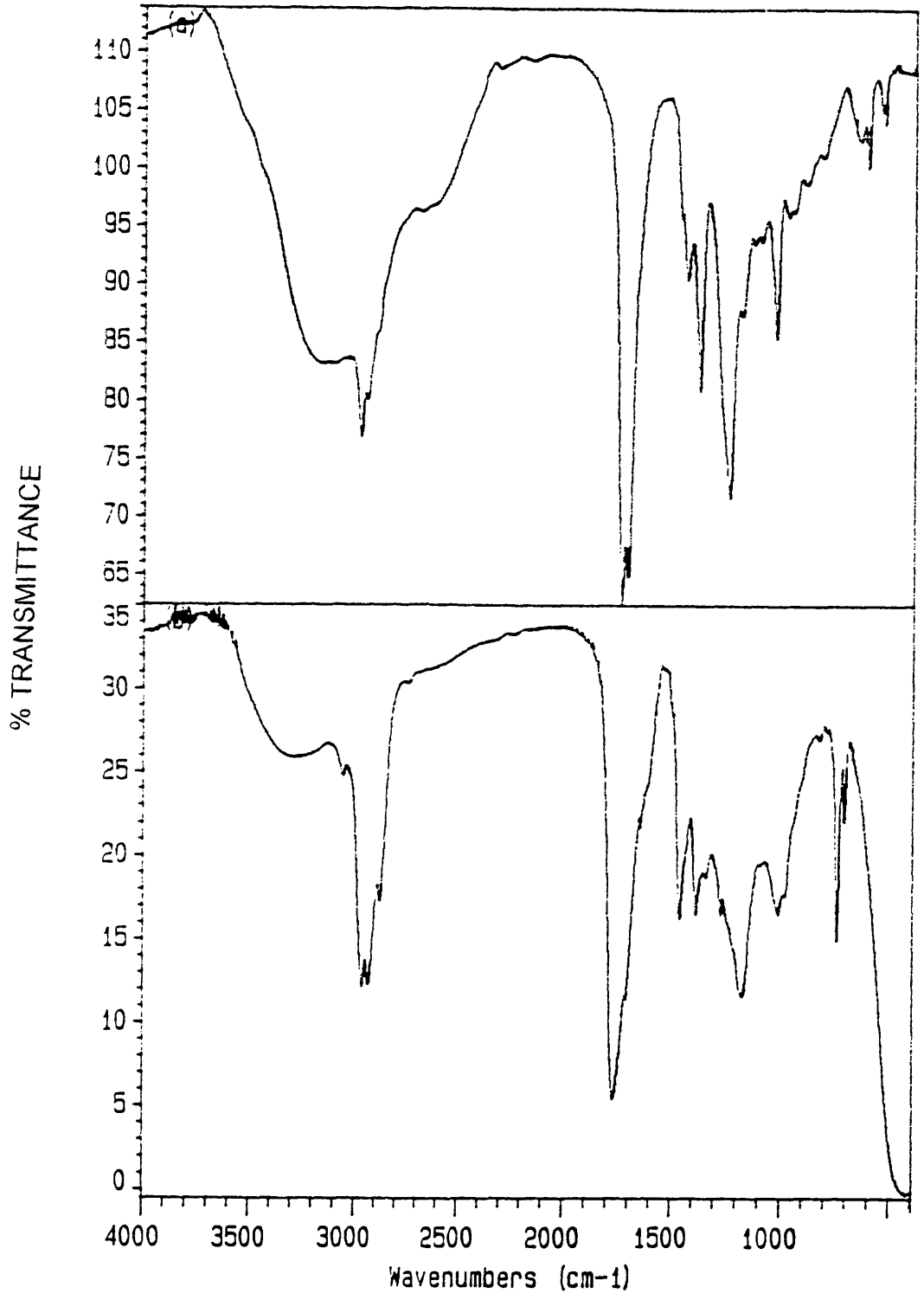


Fig. 7.5 IR spectra of (a) undegraded copolymer (b) cold ring fraction from VA—CA copolymer degraded to 500°C under TVA conditions.

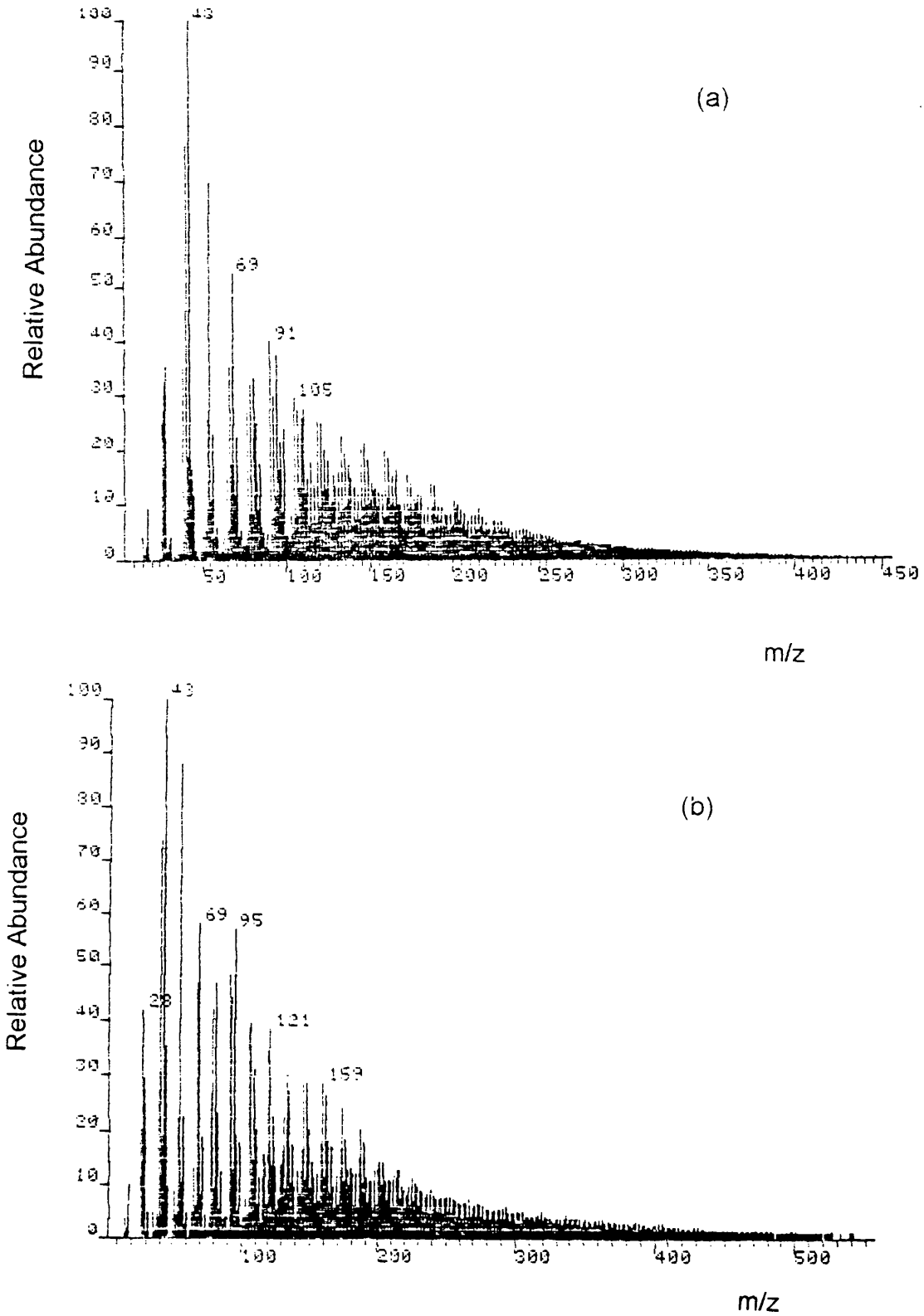


Fig. 7.6 Mass spectra for the cold ring fraction (CRF) from the degradation of VA—CA copolymer to 500°C under TVA conditions, using probe temperatures of (a) 220°C (b) 330°C.

The changes in the copolymer structure were followed by heating the film at a rate of 10°C/min to various temperatures up to the point of char. IR spectra of the cooled film were taken using reflection-absorption apparatus.

The changes in the IR spectrum of the copolymer on heating to 240, 280 and 320°C are illustrated in Fig. 7.7(b-d). The spectrum of the undegraded copolymer is presented in Fig. 7.7a, while the main absorption bands are illustrated in Table 7.5.

After heating the polymer to 240°C the following transformations can be noted. The relative intensities of the νC=O bands for the acid and ester groups change. The intensity of the acid groups decreases with only a shoulder left at 1710 cm.$^{-1}$ There is also a decrease of absorption in the OH region. A new, strong absorption appears at 1770 cm.$^{-1}$ The intensity ratio of the bands at 1170 and 1246 cm^{-1} increases suggesting that a new species is now responsible for the absorption at 1170 cm.$^{-1}$ This is corroborated by the newly appeared absorption at 1770 cm,$^{-1}$ this band suggests that the species is a γ-lactone. The ratio of the absorptions at 1460 and 1435 cm^{-1} has increased suggesting the disappearance of some CH_3 groups, probably those of the ester.

Upon heating to 280°C (Fig. 7.7c) the OH absorption at 3200-3400 cm^{-1} and the C=O absorption at 1710 cm^{-1} have completely disappeared indicating no acid groups remain. The C=O absorption at 1770 cm^{-1} has increased and the absorption at 1740 cm^{-1} is left as a shoulder. The region below 1500 cm^{-1} has become more pronounced. The ν_a C—O—C band at 1246 cm^{-1} has decreased significantly, whilst the new absorption at 1170 cm^{-1} becomes predominant confirming the decay of acetate groups and the formation of lactone. The absorption ratio of 1460 and 1440 cm,$^{-1}$ attributed

to δ CH_2 and δ_a CH_3, is more pronounced, indicating further CH_3 loss. This observation is also supported by the decreased intensity of the 1375 cm^{-1} absorption (δ_s CH_3) in Fig. 7.7(c) compared to Fig. 7.7(a). The absorption at 1375 cm^{-1} is split suggesting the appearance of new "*gem*" CH_3 groups.

Upon heating to 320°C (Fig. 7.7d) the spectrum exhibits only the lactone absorption at 1770 cm^{-1} in the carbonyl region. The ester has disappeared with its absorptions at 1740 and 1246 $cm.^{-1}$ The δ CH_2 band at 1460 cm^{-1} has overtaken δ_a CH_3 at 1440 $cm.^{-1}$ The δ CH_3 absorption formerly present at 1375 cm^{-1} is significantly diminished and is split in three bands (1385, 1375 and 1340 cm^{-1}) suggesting 2 or 3 CH_3 bound to the same C atom. It is known that the band separation indicates the type of branching (87). A band separation of 10 cm^{-1} is characteristic of isopropyl and *gem* dimethyl groups —$C(CH_3)_2$— and a band separation of 30 cm^{-1} is characteristic of the tertbutyl terminal group. In this case both separations are present, hence both types of structure must also be present. In the C—O vibration region, there is a strong absorption at 1170 cm^{-1} but the 1240 cm^{-1} band has almost disappeared.

A very small C=C absorption is present at 1640 $cm.^{-1}$ There is also a band at 990 cm^{-1} which has been present since the early stages of degradation, whose intensity is apparently increasing when compared with 1025 $cm,^{-1}$ due to skeletal vibrations. However, it is difficult to make assignments regarding the nature of the unsaturation. End chain unsaturation (vinyl type) can be ruled out as no bands are present at 910 or 890 $cm.^{-1}$ *Cis* and *trans* vinylene is the most probable structure in view of the bands present. It would be interesting to know if the unsaturation is of the trisubstituted type namely R_1 $R_2C{=}CHR_3$ which would help to establish the nature of the elimination

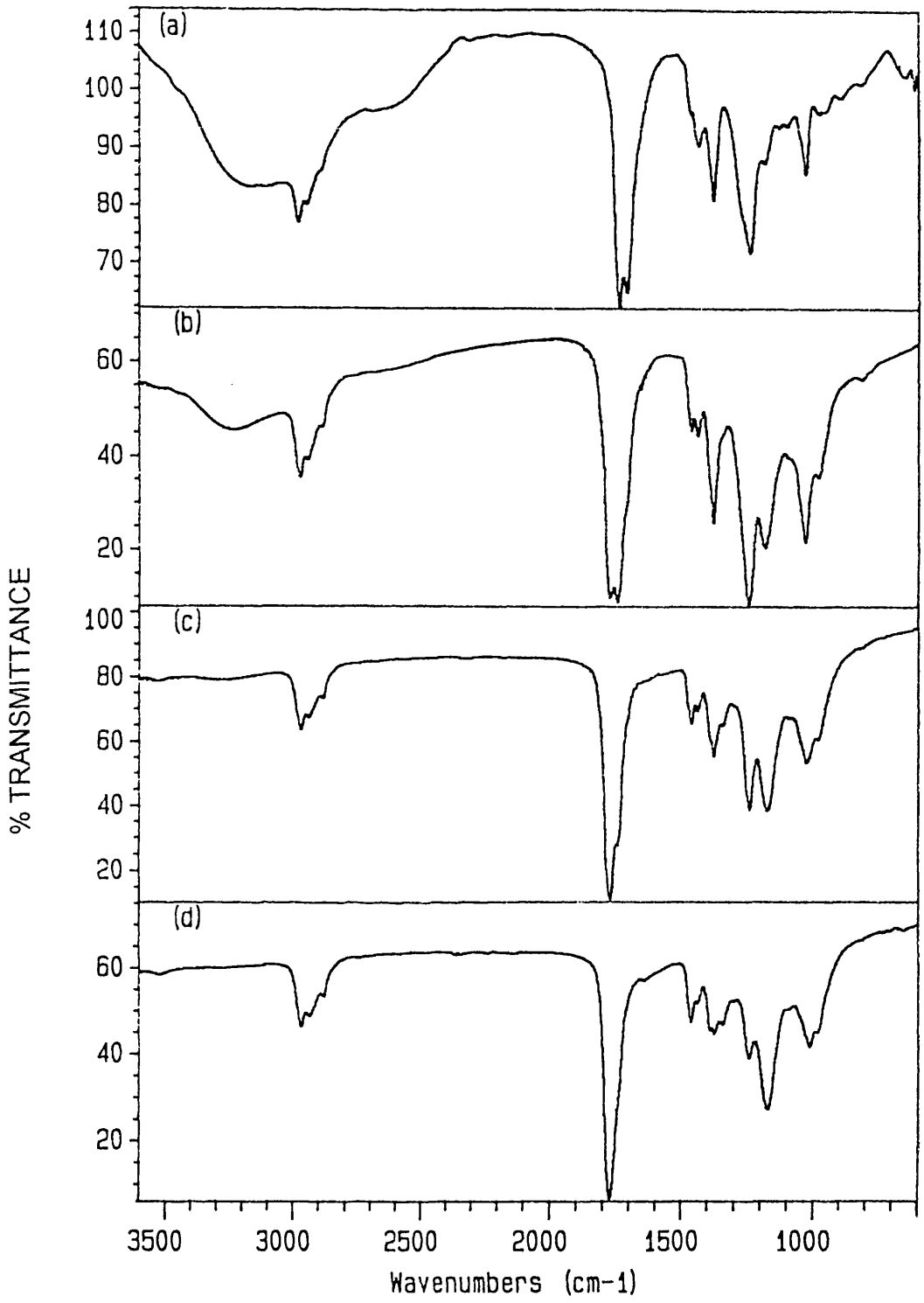


Fig. 7.7 Infrared spectra of the VA—CA copolymer: (a) before and after heating in vacuum to: (b) 240°C (c) 280°C (d) 320°C.

reactions. The trisubstituted vinylene, if present should show a band of medium intensity at 840-800 cm^{-1} which however is not observed.

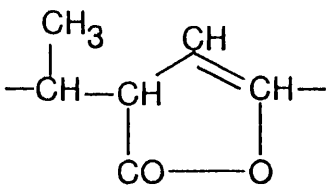
ISOTHERMAL DEGRADATION AT LOWER TEMPERATURE

In order to confirm the above FTIR findings, isothermal experiments were carried out at lower temperatures. A film was cast on a stainless steel plate then dried using the same method as described previously. The supported sample was heated in the degradation tube at 150 and 210°C under vacuum for various lengths of time, cooled down to room temperature and the spectroscopic changes at different times of heating were recorded by FTIR spectroscopy.

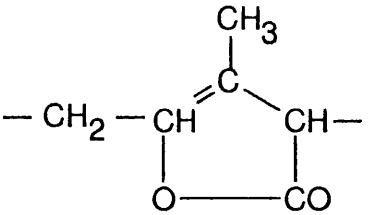
The spectroscopic changes for heating at 210°C for periods from 10 minutes to 6 hours are presented in Fig 7.8 (b-f). The spectrum of undegraded copolymer is shown in Fig. 7.8(a). As heating progresses, one can follow the disappearance of acid groups (3200-3400, 1710 cm^{-1}), ester groups (1740, 1246 cm^{-1}), CH_3 groups (1440 and 1375 cm^{-1}), the formation of new structures containing *gem* dimethyl, terminal isopropyl and terminal tertbutyl groups (by the splitting of 1375 cm^{-1} band); the relative increase of the content of CH_2 groups (1460 cm^{-1}) and the appearance of unsaturation (1640 cm^{-1}). At prolonged heating, over 220 min, the position of the lactone band changes to 1778 $cm.^{-1}$ The band has a peculiar shape making it possible to infer the presence of a shoulder at 1770 $cm.^{-1}$ This is difficult to explain unless one admits the formation of unsaturated lactones of the structures I or II illustrated, which would also be expected to give a weak band at 1660 (1640 cm^{-1} in our case) (88). The formation of the band at 1640 $cm,^{-1}$ however, precedes the displacement of the band at 1770 to 1778

cm.$^{-1}$ Hence, there is also some other type of unsaturation in the system, apart from the unsaturated lactone.

Structure I



I



II

In order to compare the changes in the above absorbances they have to be related to an internal standard. Although it is difficult to find a band whose intensity does not change during the thermal degradation and can be taken as an internal standard, such a band was selected as ν_a CH_2 at 2930 cm.$^{-1}$ The justification is offered by the experimental observation that the intensity ratios of the bands of the CH_3 to the CH_2 groups in the 2800-3000 cm^{-1} region, namely 2970/ 2930 and 2885/ 2930 cm^{-1} stay remarkably constant as other ratios involving the same groups: 1440/ 2930, 1380/ 2930 cm^{-1} vary as in Figures 7.9 and 7.10 during the isothermal degradation at selected temperatures up to 210°C. The intensity ratio of the bands of the CH_2 1460/2930 remains constant at 150°C and slightly decreases at 210°C. Although this is difficult to explain without being highly speculative, it can be used to advantage in following the change in the concentration of various groups, by taking the CH_2 group as an internal standard. Figures 7.9 and 7.10 presents the variation of the intensity ratios of the bands specific to the groups of interest to the intensity of the ν_a CH_2 (2930 cm^{-1}) band with the time of heating at the temperatures of 150 and 210°C, respectively.

The behaviour observed in Fig 7.9 shows that the ester and acid groups disappear as the lactone is formed. The ester and acid groups disappear

with roughly the same rate at 150°C. The decay of CH_3 groups at this temperature is related to the elimination of the ester groups. At 210°C (Fig. 7.10) the formation of the lactone cannot be even followed and the curve shows only the decomposition after a plateau which ends at 50 min. The acid groups disappear at a fast rate. Practically, after 20 min they cannot be seen even by subtraction of spectra. The ester groups decay at a lower rate, some remaining behind long after the acid groups have vanished. About 30 % of the ester groups remain to decay alone after the acid groups are gone as shown by curve 1. This implies that the acid groups undergo another reaction competing with lactone formation. CH_3 groups decay initially at a fast rate during the first 20 min, probably those belonging to the ester function which are lost through lactone formation. Subsequently there is a slower decay and a levelling off. In the original VA—CA copolymer, 50% of the CH_3 groups are branches in the crotonic acid units and 50 % belong to the ester groups, if one ignores the contribution of the chain ends. One can compute on curve 5 of Fig. 7.10 that about 35 % of all CH_3 groups are lost in the first 20 min i.e. through lactone formation, which make again 70 % of the CH_3 groups belonging to the ester groups. About 30 % remain to decay at a slower rate. Curve 5 attains a plateau after 200 min at 210°C leaving 25% of the total CH_3 groups. That means that about 50% of the CH_3 in the crotonic units have also decayed. Since no other major volatile products are observed, this suggests that some of the original crotonic acid groups must appear in the cold ring fraction products, which make up almost half of the total decomposition products. The above figures are considered only orientative. More precise figures describing the extent of transformations can be obtained only by the use of a real internal standard.

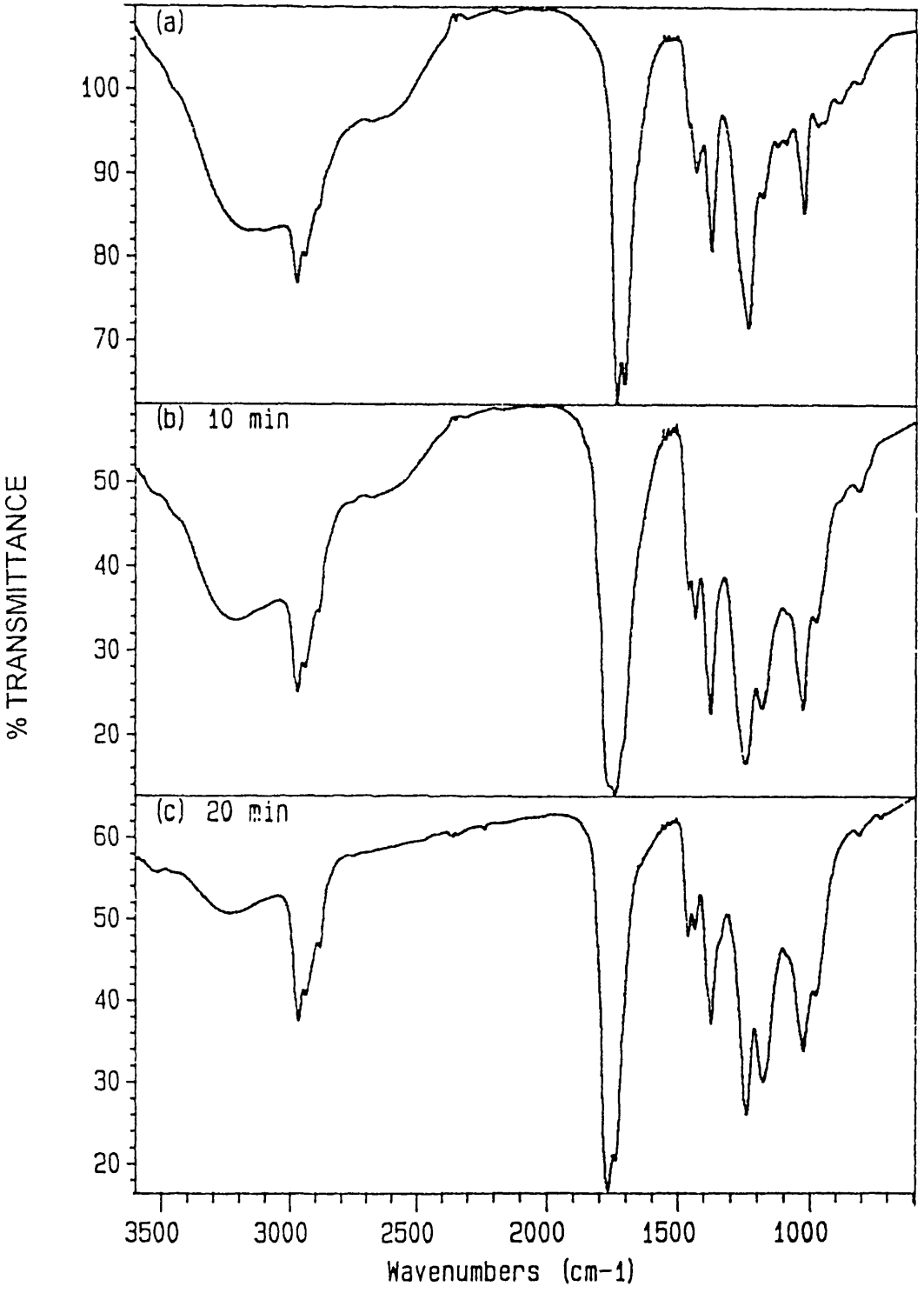


Fig. 7.8 Infrared spectra of the VA—CA copolymer: (a) before and after heating in vacuum at 210°C (b) 10 min (c) 20 min.

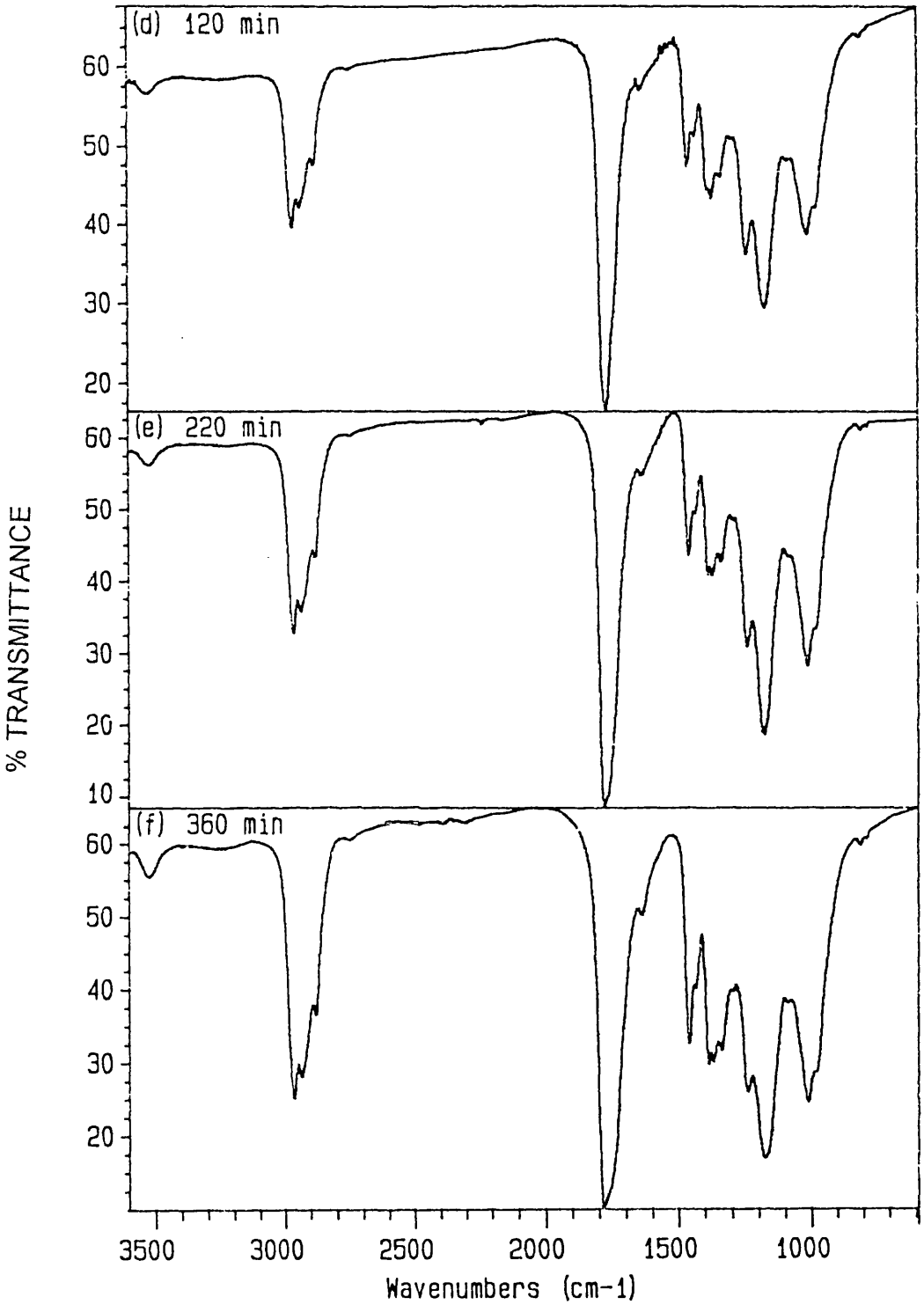


Fig. 7.8 Continued (d) 120 min (e) 220 min (f) 360 min.

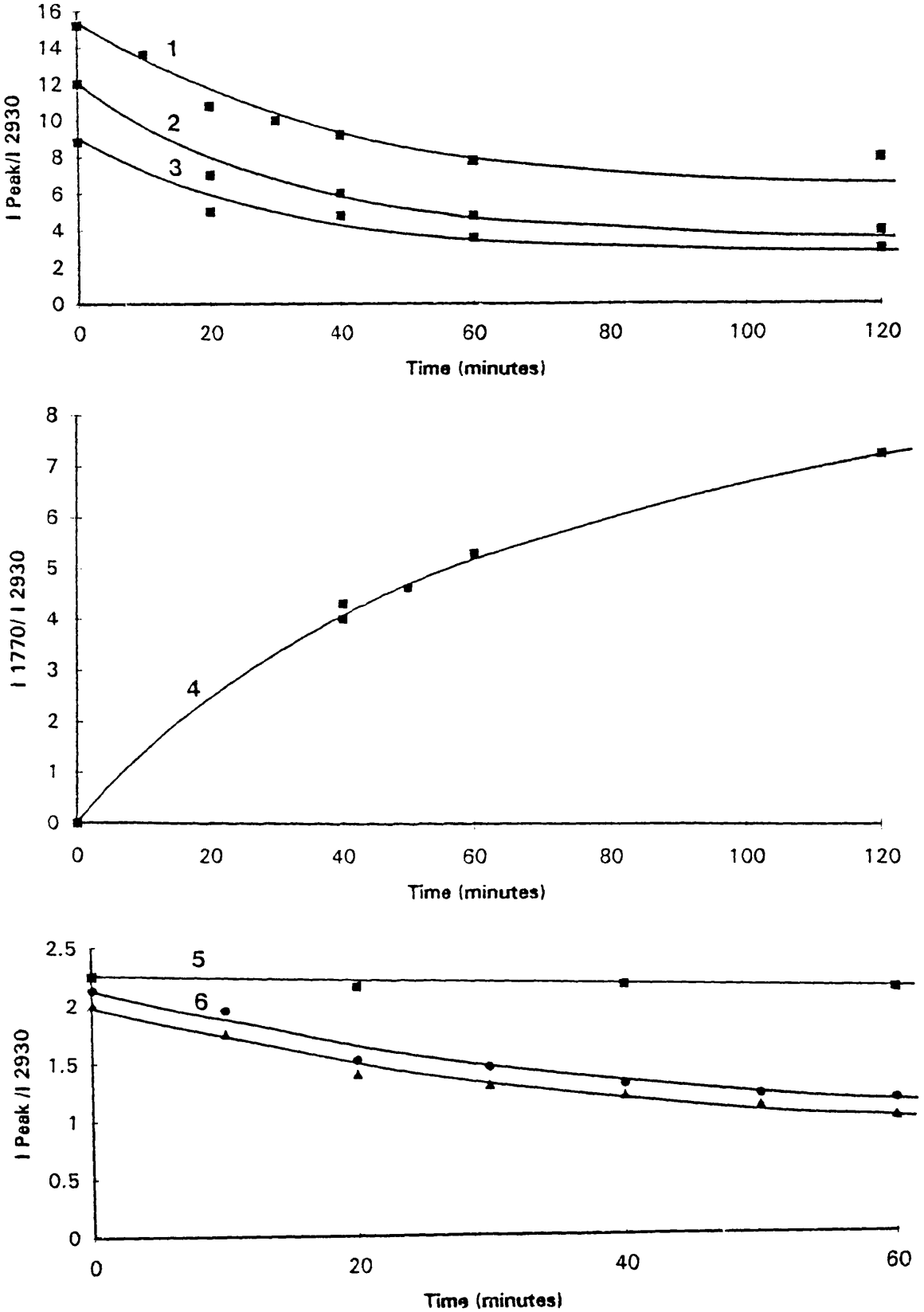


Fig. 7.9 Intensity ratios of the main bands in the IR spectrum relative to the band at 2930 cm^{-1} as a function of time of heating at 150°C.
Key to curves: 1, ester, 1740 cm^{-1} ; 2, acid, 1710 cm^{-1} ; 3, ester, 1240 cm^{-1} ; 4, lactone, 1770 cm^{-1} ; 5, CH_2, 1460 cm^{-1} ; 6, CH_3, 1440 (•), 1380 (▲) $cm.^{-1}$

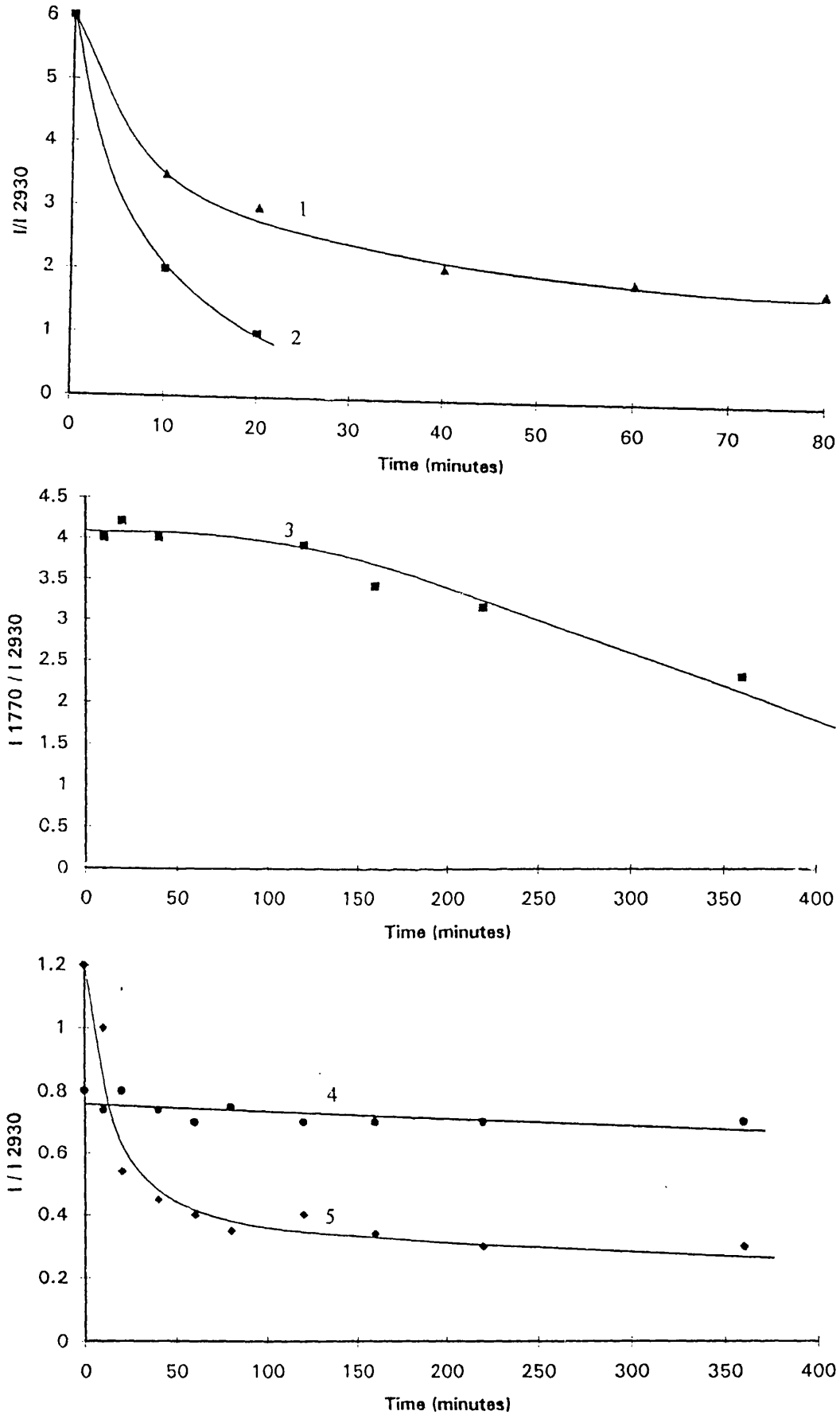


Fig. 7.10 Intensity ratios of the main bands in the IR spectrum relative to the band at 2930 cm^{-1} as a function of time of heating at 210°C.
Key to curves: 1, ester, 1740 cm^{-1} ; 2, acid, 1710 cm^{-1} ; 3; lactone 1770 cm^{-1} ; 4, CH_2, 1460 cm^{-1}; 6, CH_3, 1440 $cm.^{-1}$

DISCUSSION

The degradation of VA—CA alternating copolymer differs significantly from the reaction mechanism of the vinyl acetate homopolymer. The detailed study of vinyl acetate homopolymer has been described in Chapter 4. PVA degrades in two well defined stages under programmed heating, first losing acetic acid progressively to form conjugated polyene sequences, and then by further reaction including chain fragmentation at higher temperatures, leaving some char residue (26, 68).

In the alternating copolymer of VA and maleic anhydride, a similar deacetylation reaction occurs first at the VA units, followed by the fragmentation of the modified chain (33). The degradation of VA—CA differs with respect to the possibility of inter-unit reaction by cyclisation to form lactone rings, a reaction which occurs at lower temperature than deacetylation of the VA units (82).

In the light of the above experimental results, the mechanism of the thermal degradation for the alternating VA—CA copolymer can be advanced (scheme 1-6).

In the first stage, the main reaction is cyclisation of adjacent acetate and acid side groups with the elimination of acetic acid and the formation of γ-lactone rings. In a secondary reaction, decarboxylation of acid groups occurs with the elimination of carbon dioxide. Because methyl substituents appear only on every fifth backbone carbon in this copolymer structure, there are two possible ways for lactonisation to occur. Furthermore, the cyclisation between adjacent reacting units occurs at random and can therefore leave isolated acid side groups so that the intermediate copolymer product from partial degradation in this case is not structurally regular.

In the second stage, the main reaction is lactone decomposition leading to extensive chain scission.

This mechanism is supported by the analysis of the FTIR spectra. The acid groups in the copolymer disappear first. Some ester groups remain behind for some time until they disappear completely and unsaturation is formed.

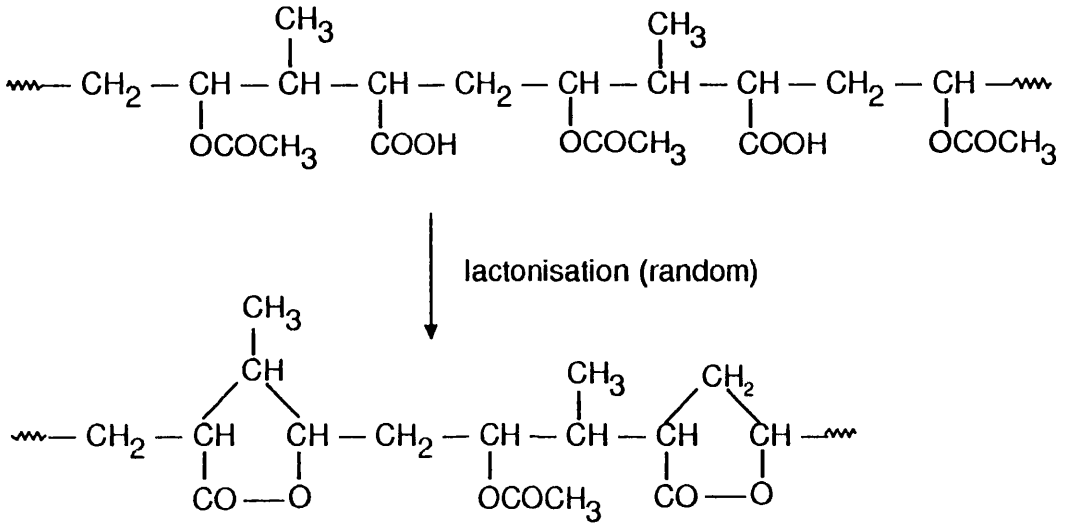
Carboxylic groups could also decay through a parallel reaction. The decarboxylation reaction is known to generate alkanes (89) and if present in our system (Scheme 2) could explain the presence of products with long aliphatic chains.

However, the major reaction is the lactone formation and it is the major source of acetic acid. Lactone formation also takes place in VA—MMA copolymer through the elimination of methyl acetate (68) and with greater ease in VC—MMA copolymers through the elimination of methyl chloride (43, 90). Both of these copolymers show this side group lactonisation reaction as the main degradation route at lower temperatures. Even in blends of PVA and PMMA the PMMA is destabilised through the attack of the migrating acetoxy radicals and methyl acetate is eliminated (90).

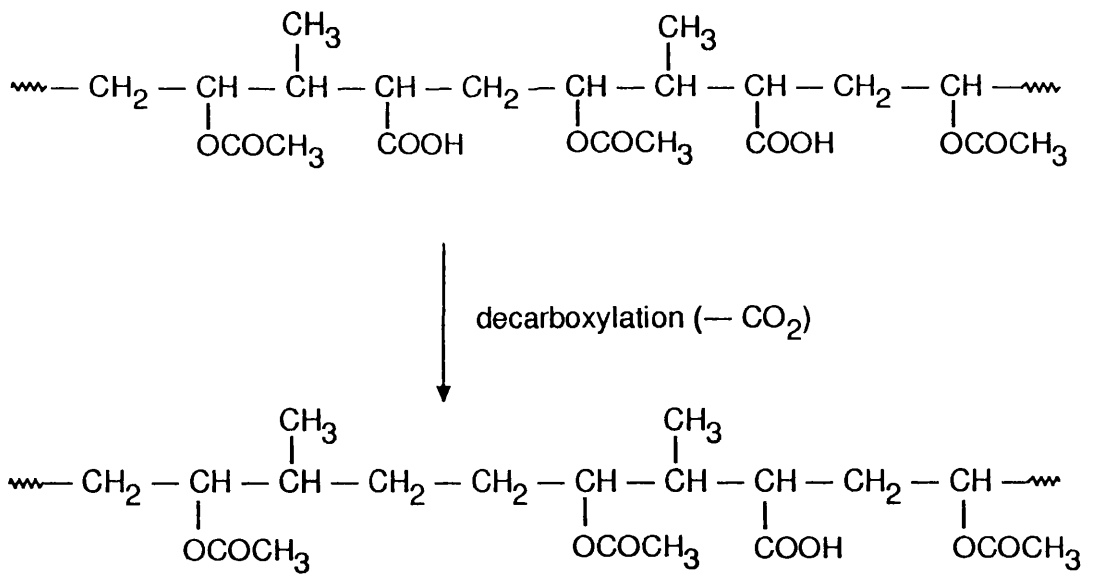
The decomposition of the lactone through Scheme 3 is the major source of carbon dioxide. It also explains the backbone scission which results in the complete degradation of the polymer in 30 min at 320°C leaving practically no tar. As a general rule, aliphatic lactones are known to decompose giving CO_2 and alkene. This type of decomposition has been used as a method of preparing alkenes with the retention of the geometry they had in the lactone (91). With lactone formed along the macromolecular chain the situation might be different. All the polymers known to produce lactone suffer

Mechanism for thermal degradation of CA—VA alternating copolymer

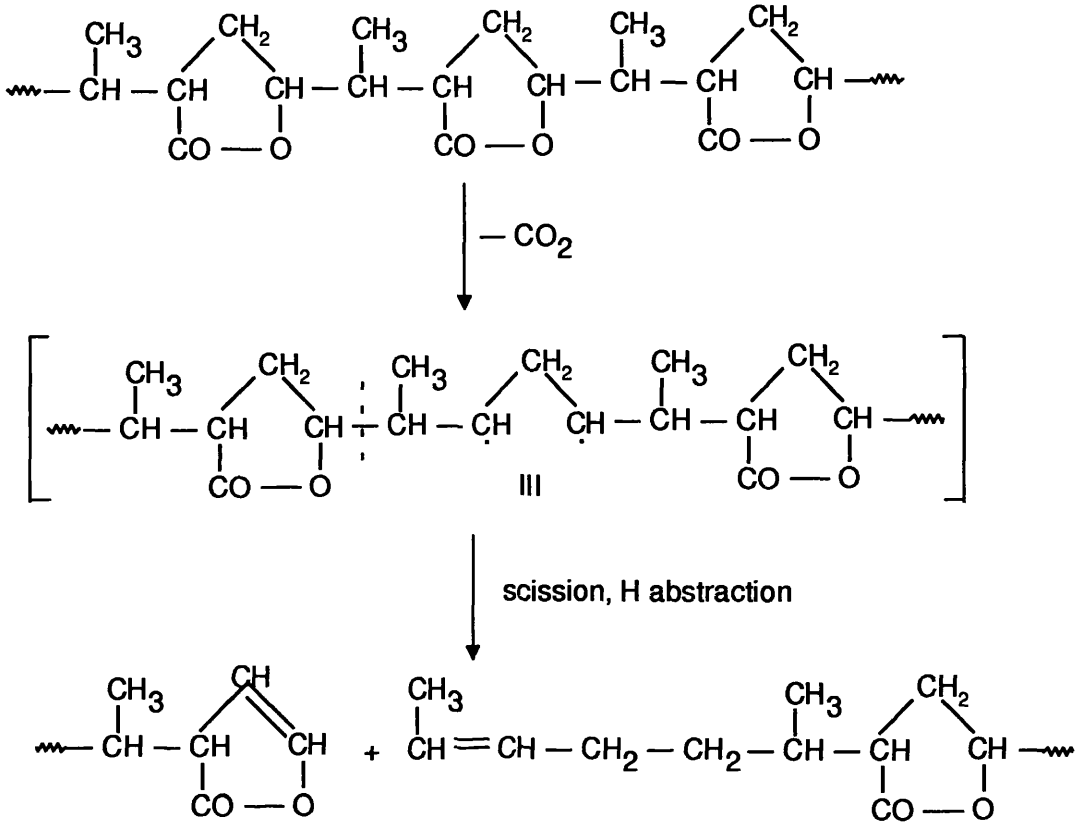
Scheme 1



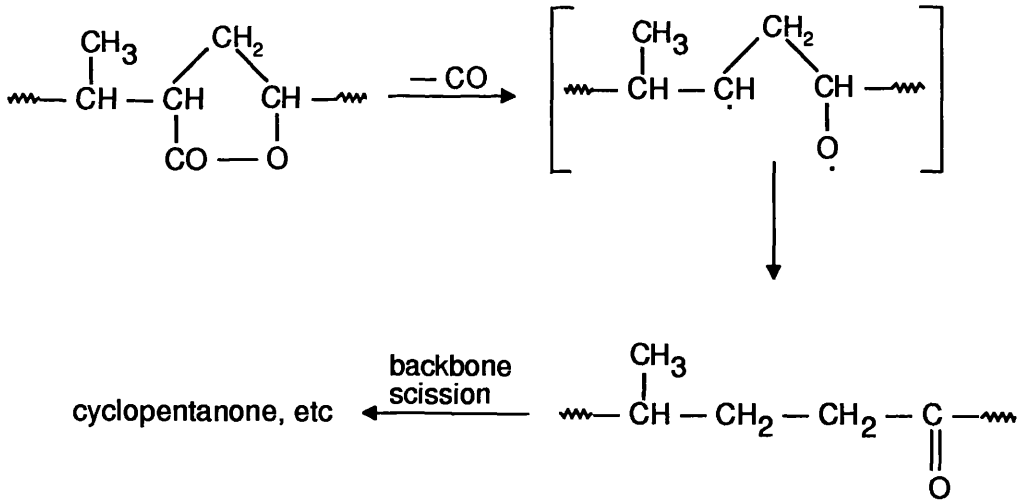
Scheme 2



Scheme 3



Scheme 4



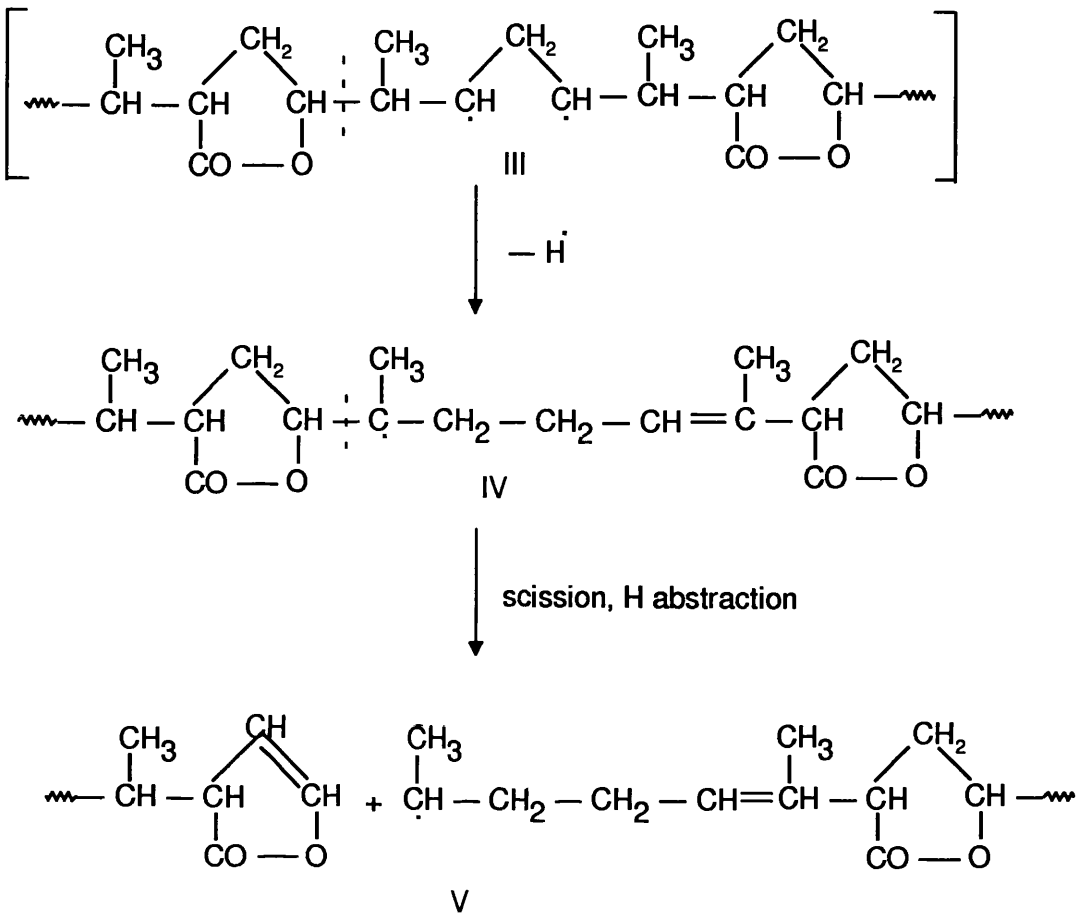
frequent scissions at higher temperatures, along with the formation of CO_2 and some CO (68, 90).

Our experimental data are consistent with scission of the diradical intermediate in the decomposition of the lactone. Had the decomposition of the lactone led to the formation without backbone scission of unsaturation along the polymer chain, the polymer would produce a high fraction of crosslinked tar, which is not the case. Also there is very little unsaturation shown in the IR spectrum of the degraded polymer. Similarly, aromatic volatile products are formed in minor amounts.

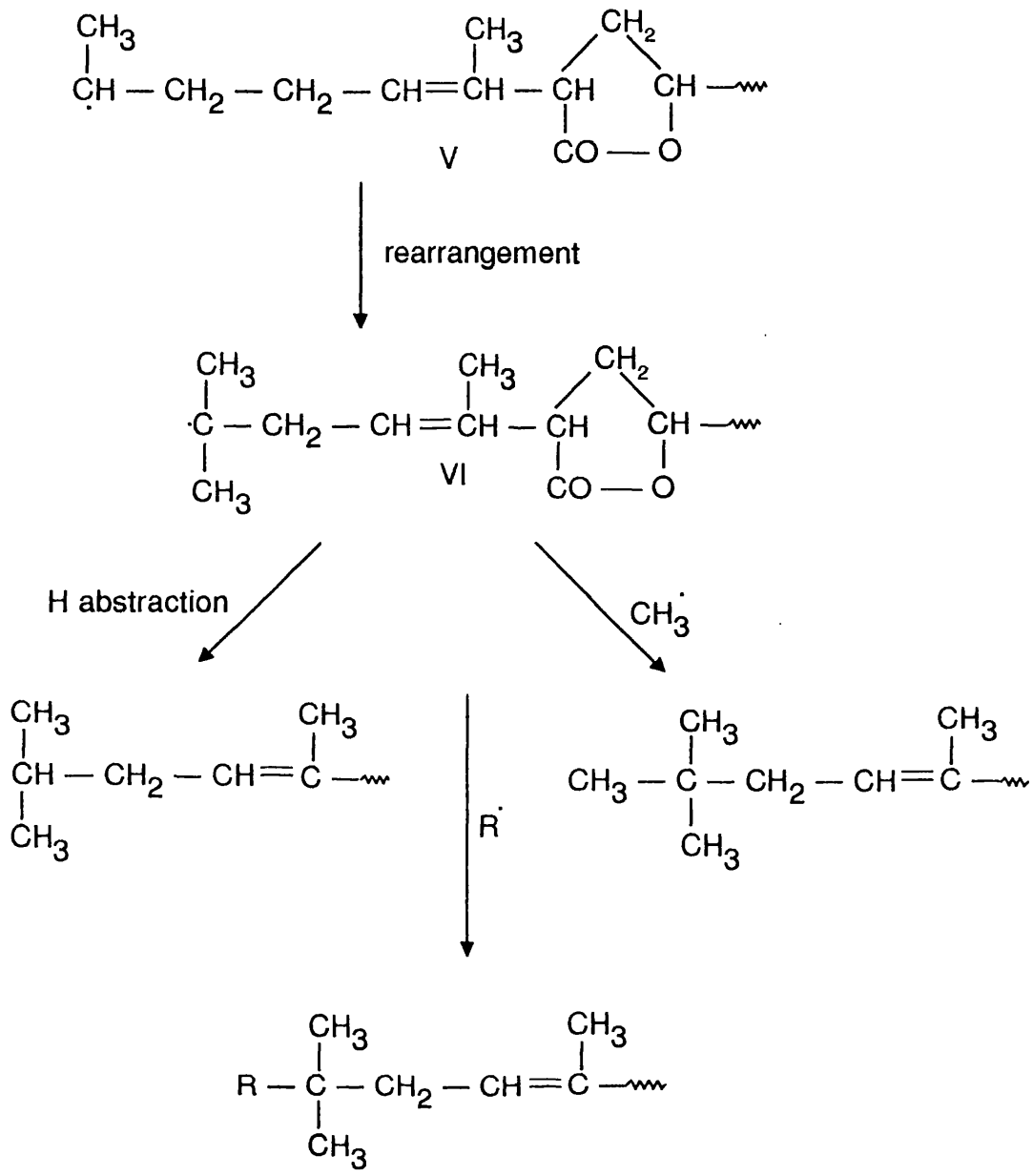
This situation is entirely different from that in the degradation of PVC, which gives a high fraction of aromatic hydrocarbons many of them with condensed rings and considerably more tar (21) or even from degradation of PVA which gives similar aromatic products and tar (26,68). The presence of small amount of ketones in the system may be due to loss of CO by Scheme 4 and subsequent backbone scissions.

Additional information on the fate of acid and ester groups can also be interpreted from the DSC and TG curves Figs. 7.1 & 7.2 respectively. During the first stage of degradation, 200-310°C in the TG and DSC curves, there is a weight loss of 33% associated with a large endotherm. A weight loss of 8% corresponding to the small endotherm (between 200 and 240°C) which is not resolved from the large endotherm. Since only acetic acid (abundant) and CO_2 (minor) were identified, it is clear that the large endotherm is due to the acetic acid elimination through lactone formation and a small endotherm is due to the decarboxylation of some of the crotonic acid units. It can be calculated from the weight loss of 8% associated with the decarboxylation that one in three crotonic acid units decarboxylate.

Scheme 5



Scheme 6



This rather high proportion explains the rapid disappearance of the acid groups and the appearance at higher temperatures of products with straight aliphatic chains. The remaining two-thirds of the acid groups decay by lactonisation.

The ester groups have a higher temperature resistance than the acid groups. This can be seen from the DSC thermogram of PVA (Fig. 4.2, chapter 4) and it is also shown in the IR spectra in which the ester absorption is present until more advanced stages of degradation. In Fig. 4.2, Chapter 4, the large endotherm at 260-360^{o}C is due to the zip deacetylation of PVA and the small endotherm at 360-400^{o}C is probably due to the deacetylation of the groups remaining after the zip reaction. In the case of the VA—CA copolymer, the deacetylation of the ester groups remaining after lactonisation is shifted to lower temperatures, 310-350 ^{o}C. There is a weight loss of 12.5% in this temperature interval. Considering the structure of the copolymer in which 1/3 of the acetate groups have survived lactonisation, 2/3 have lactonised and 1/3 of the COOH groups have suffered decarboxylation, one can calculate the acetate group content as being 15.4%. Consequently most of the acetate groups (12.5%) are lost in this temperature interval. These conclusions are in very good agreement with the estimations made from the decay of various groups on the basis of their IR absorbances.

The IR spectral changes during degradation show the appearance of isopropyl and tertbutyl end groups and, possibly, the formation of *gem* dimethyl groups. The presence of these structures can be explained (Scheme 5) if rearrangement (92) and H-elimination occurs in the biradical III formed through the decomposition of the lactone, to produce radical IV. Through this rearrangement, a secondary radical is converted into a tertiary radical by H transfer to a neighbouring position, forming a

thermodynamically more stable species. Radical IV, by scission in the a position to the lactone and the radical V. The latter secondary radical by rearrangement can be converted to the more stable radical VI, (92) which in turn can undergo the reactions shown in Scheme 6, explaining the formation of the isopropyl, tertbutyl and *gem* dimethyl structures.

CONCLUSIONS

The thermal degradation of the alternating 1:1 vinyl acetate-crotonic acid copolymer under dynamic heating presents two stages. In the first stage extensive γ-lactone formation occurs through a reaction between ester and acid groups eliminating acetic acid. It has been evaluated that 2/3 of the ester and acid groups participate in lactone formation. Approximately 1/3 of the acid groups suffer decarboxylation leaving aliphatic sequences on the polymer backbone and 1/3 of the ester groups survive the first stage of degradation. In the second stage the main reaction is lactone decomposition leading to frequent scissions, which produce a substantial fraction (47% by weight) of cold ring products consisting essentially of fragments of partially degraded copolymer containing mainly lactone rings but with sections of aliphatic chain (such as from decarboxylation). Practically, the polymer degraded leaving no tar. The products formed in this stage are CO_2, non-condensable gases (CO, CH_4), and various minor products, consisting of C_3 and C_4 carboxylic acids, cyclopentanone and unsaturated cyclic and acyclic ketones and hydrocarbons.

As it degrades, the polymer shows little unsaturation, associated mainly with the presence of unsaturated lactones. It shows chain branching as the main macroradical rearrangement after scission. The split radicals disproportionate to give alkenes and alkanes, or cyclize to give cycloalkene and cycloalkanes and aromatic rings. Most of the cycloalkene and cycloalkane rings bear ketone groups. These groups are formed from the

acetate groups which have survived the first stage of degradation. In the second stage they suffer the scission of the ester bond giving pendant alkoxy radicals which form ketones. Other reactions of the acetate groups are: terminal alkoxy formation (very active in cyclization leading to furan type rings) and acetic acid elimination forming unsaturation. Under isothermal heating this second stage develops in time with no sharp transition and its start depends on the temperature of the degradation.

Compared to poly(vinyl acetate) the CA—VA copolymer has lower resistance to thermal degradation. It differs from the VA—maleic anhydride alternating copolymer in giving acetic acid as the main product primarily by lactone formation involving cyclisation between the adjoining VA and CA units rather than by deacetylation of the VA units.

CHAPTER EIGHT

THERMAL DEGRADATION STUDIES OF POLY(ISOPROPENYL ACETATE)

AIM OF THE PRESENT WORK

In the present work, the thermal degradation of poly(isopropenyl acetate) (PIPAc) has been investigated by using TVA, TG and DSC techniques to establish the thermal degradation mechanism of the polymer. The thermal degradation in vacuum up to 500°C has also been studied by following the relative rate of volatile product formation in thermal volatilisation experiments and by monitoring at the same time the formation of the main products by mass spectrometry coupled to the TVA system. The basis of this procedure has been described in detail in Chapter 2.

Quantitative measurements of the main product fractions (liquid fraction and condensable bases, cold ring fraction and residue) have been made. The non-condensable gases were calculated by difference. The condensable products from the TVA degradation have been analysed by IR, MS and GC-MS technique.

The non-condensable products formed during degradation were identified by using the mass spectrometer on-line to the TVA apparatus.

The poly(isopropyl acetate) sample was prepared as described in Chapter 3 and the preparation conditions are listed in Table 8.1. The thermal degradation of poly(isopropenyl acetate) has been investigated by the degradation techniques described below.

Table. 8.1. The preparation conditions of poly(isopropenyl acetate) by free radical polymerisation.

Amount of isopropenyl acetate	50 g
Amount of initiator (AIBN)	0.1%*
conversion	6.5%
Time of polymerisation	12 hours
Temperature of polymerisation	60°C
Conversion	5.8%

* Relative to the total weight of monomers

THERMOGRAVIMETRIC STUDIES

The thermogravimetric (TG) and differential thermogravimetric (DTG) behaviour of poly(isopropenyl acetate) was obtained under dynamic nitrogen at a heating rate of 10°C/min. The data presented in Fig. 8.1 indicate three stages of polymer break down. In the early stage of heating between 60 and 110°C, there is small weight loss in the TG diagram due to the expulsion of some residual precipitant (n-hexane).

In the first and major stage of decomposition, between 160 and 250°C, there is a weight loss of 60% corresponding to the theoretically total loss of acetic acid in the polymer. However the IR spectrum of partially degraded polymer suggests that a very small fraction of acetate groups survive up to 400°C.

Between 250 and 350°C the polymer loses 10% of its weight at a steady and slow rate. This will be called a second degradation stage for reasons which will be discussed later.

The third stage of decomposition between, 350 and 475°C is accompanied by 20% weight loss. The methyl-substituted unsaturated hydrocarbon chain formed mainly in the first stage and subsequently in second stage suffers extensive fragmentation in the temperature region of 350°C to 500°C.

The TG curve indicates an insignificant amount of residue at 500°C for poly(isopropenyl acetate).

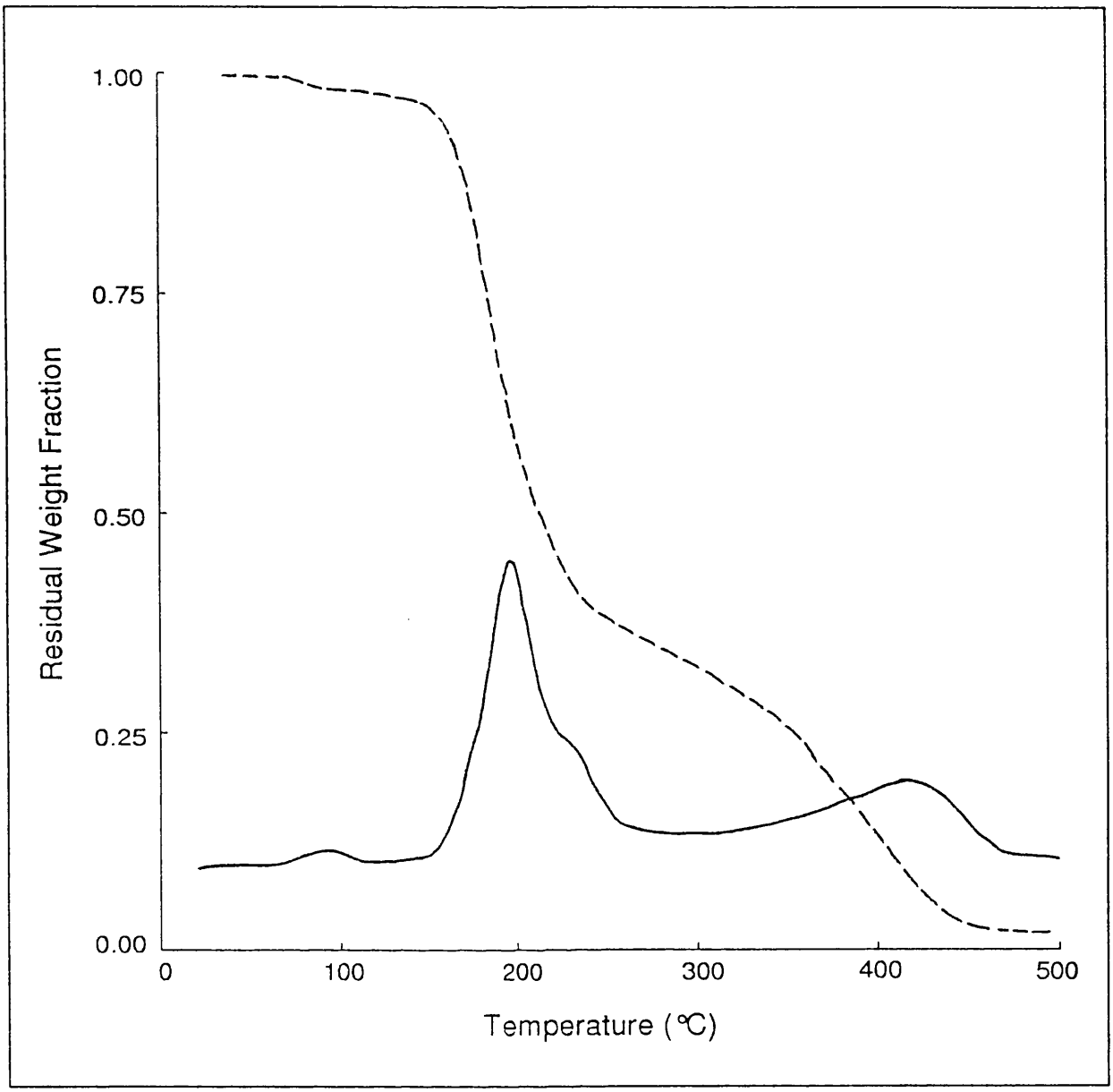


Fig. 8.1 TG and DTG curves obtained for PIPAc (heating rate 10°C/min, nitrogen flow).

DIFFERENTIAL SCANNING CALORIMETRY

The thermal stability was also examined by differential scanning calorimetry (DSC) in the range of 30°C to 500°C under dynamic nitrogen. The DSC curve for poly(isopropenyl acetate) is illustrated in Fig. 8.2.

The DSC curve shows two distinct endotherms: one major endotherm between 150 and 250°C, with the thermal effect of 320J/g. This deep endotherm corresponds to the major weight loss of 60% in the first stage of decomposition indicated in the TG curve (Fig. 8.1).

In the temperature region 255°C to 330°C there is a shallow endotherm in the DSC curve with the thermal effect of 17J/g. This endotherm corresponds to the steady decomposition indicated in the TG curve (weight loss of 10%) which has been referred to as second stage. There is no endotherm corresponding to the third stage of decomposition indicated by the TG curve (weight loss of 20%). The heat capacity of the sample decreases continuously in this temperature region due to the changes in the polymer structure.

THERMAL VOLATILISATION ANALYSIS

The polymer sample was subjected to TVA under continuous evacuation as described in Chapter 2. The TVA curve for PIPAc is presented in Fig. 8.3.

The polymer degradation in vacuum up to 500°C has been followed by recording the relative rate of volatile product formation according to the procedure of thermal volatilisation analysis (TVA) while also monitoring by mass spectroscopy the formation of the main degradation products.

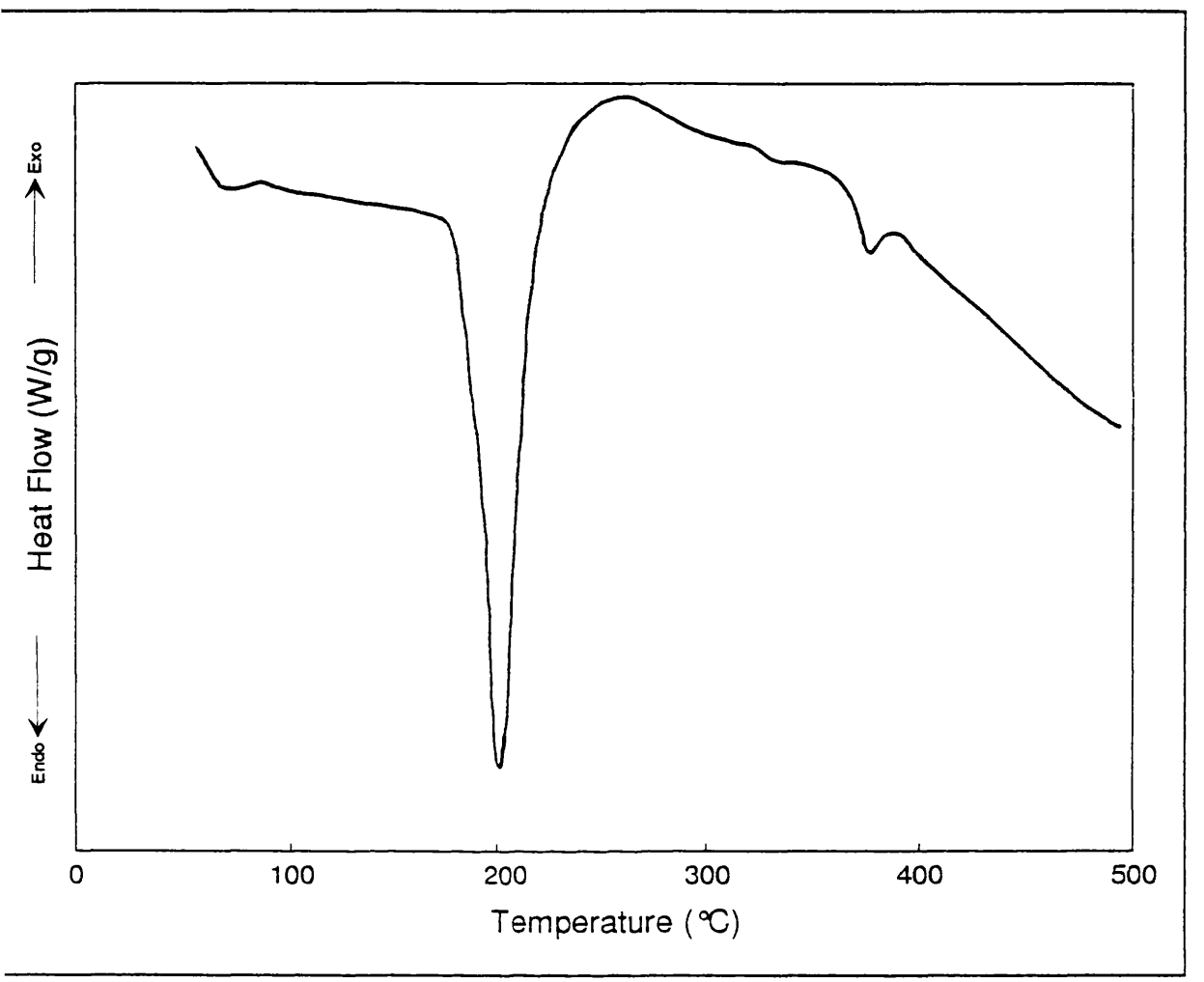
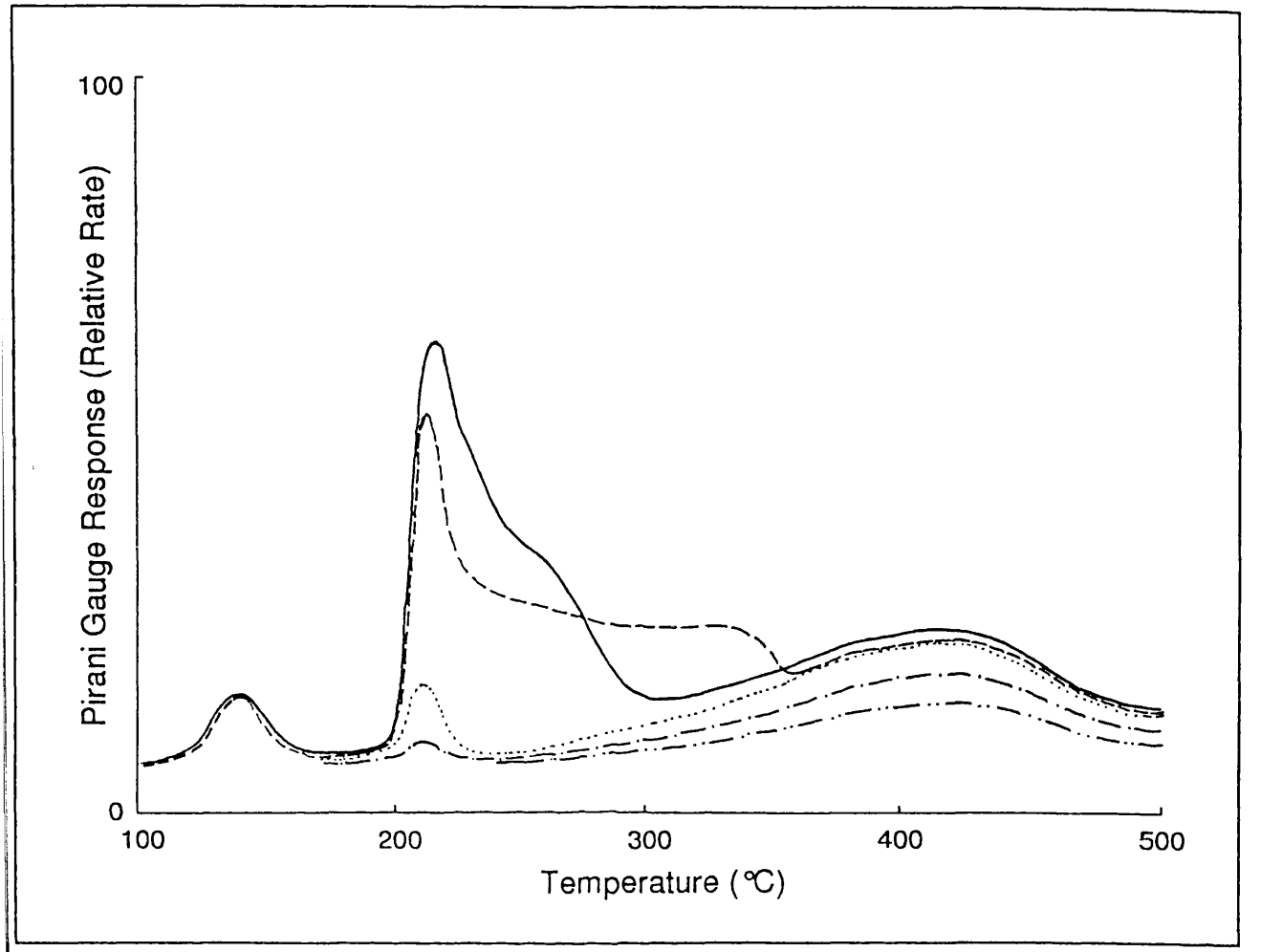


Fig. 8.2 DSC curve for PIPAc (heating rate 10°C/min under nitrogen flow).

The TVA curve for PIPAc also indicates the three stages of polymer breakdown. The first, which is the main decomposition stage, takes place between 160 and 250°C. The second stage, can be seen as a shoulder in the temperature region 250-350°C. The third stage of decomposition is well defined in the temperature region 350-500°C both in TG and TVA traces.

The TVA traces (Fig. 8.3) are due to the presence of various degradation products escaping the traps. Trace 1 is mainly due to acetic acid escaping the trap at 0°C. Trace 2 is mainly due to aromatic hydrocarbons escaping the trap at -45°C, but also to the small effect of acetic acid sublimation described by Jamieson & McNeill (68). Trace 3 is due to ketene and other compounds of low boiling point which escape the trap at -75°C under vacuum. Trace 4 due to a minor amount of alkenes and alkanes formed through pyrolysis and trace 5 is due to the non-condensable gases (CO, H_2, CH_4). As can be seen from Fig. 8.3, acetic acid is formed mainly in the first two stages and in very small amount in third stage, if any. The production of the aromatic fraction is difficult to evaluate from the TVA curve, but is easily evaluated through ion monitoring by MS. Ketene is formed in an important amount in the first stage and even more in the third stage. There is a very small fraction of non-condensable gases, formed only in the third stage of decomposition, as shown in the TVA trace.

At the end of TVA experiment, the fractions of different volatility produced by pyrolysis were quantitatively determined by direct weighing. The results are presented in Table 8.2. The major products consist of condensed volatile material (61%) and the cold ring fraction (37.5%), so that the amount of gases and residue are negligible.



Key

0°C
-45°C
-75°C
-100°C
-196°C

Fig. 8.3 TVA curve for PIPAc sample heated in vacuum to 500°C at 10°C/min.

Table 8.2 The material balance of the fraction collected during the degradation to 500°C of the PIPAc under TVA conditions

No	Fraction	%
1	Condensable gases and liquid fraction	61
2	Cold ring fraction (tar)	37.50
3	Residue	> 1
4	Non-condensable gases (by difference)	> 1

The evolution of the major degradation products was followed by plotting the intensity of their characteristic ions recorded by the mass spectrometer versus time (temperature) as shown in Fig. 8. 4(a-e). The product of the first stage of decomposition is mainly acetic acid which begins to form around 160°C in the process of deacetylation. The acetic acid is accompanied by some ketene and water. Fig. 8.4a shows the formation of acetic acid as indicated by its fragmented ions (m/e 45, 60) and ketene (m/e = 42). As can be seen, these two products are formed simultaneously.

Between 250 and 350°C, the unsaturated chain formed due to the elimination of acetic acid begins to generate aromatic hydrocarbons. This process takes place due to scission of the substituted unsaturated hydrocarbon macromolecular chain, and produces only light aromatic compounds and smaller amount of methylsubstituted aliphatic unsaturated hydrocarbons.

The third degradation stage (350-500°C) is the temperature region where more extensive fragmentation of the unsaturated hydrocarbon backbone takes place. A higher fraction of aromatic compounds is formed in this temperature region. The major part of the cold ring fraction (CRF) is formed mainly in this stage of decomposition.

The Fig. 8.4b illustrate the formation of toluene as indicated by characteristic ions m/e = 91 and 92. Fig. 8.4c shows the formation of 1,3,5-trimethyl benzene (e/m = 105, 120) which is the major component of the liquid fraction (Table 8. 4) after acetic acid. This figure also presents the formation of 1,2,6-trimethylbenzene identified by GC-MS as a liquid fraction product (Table 8.4).

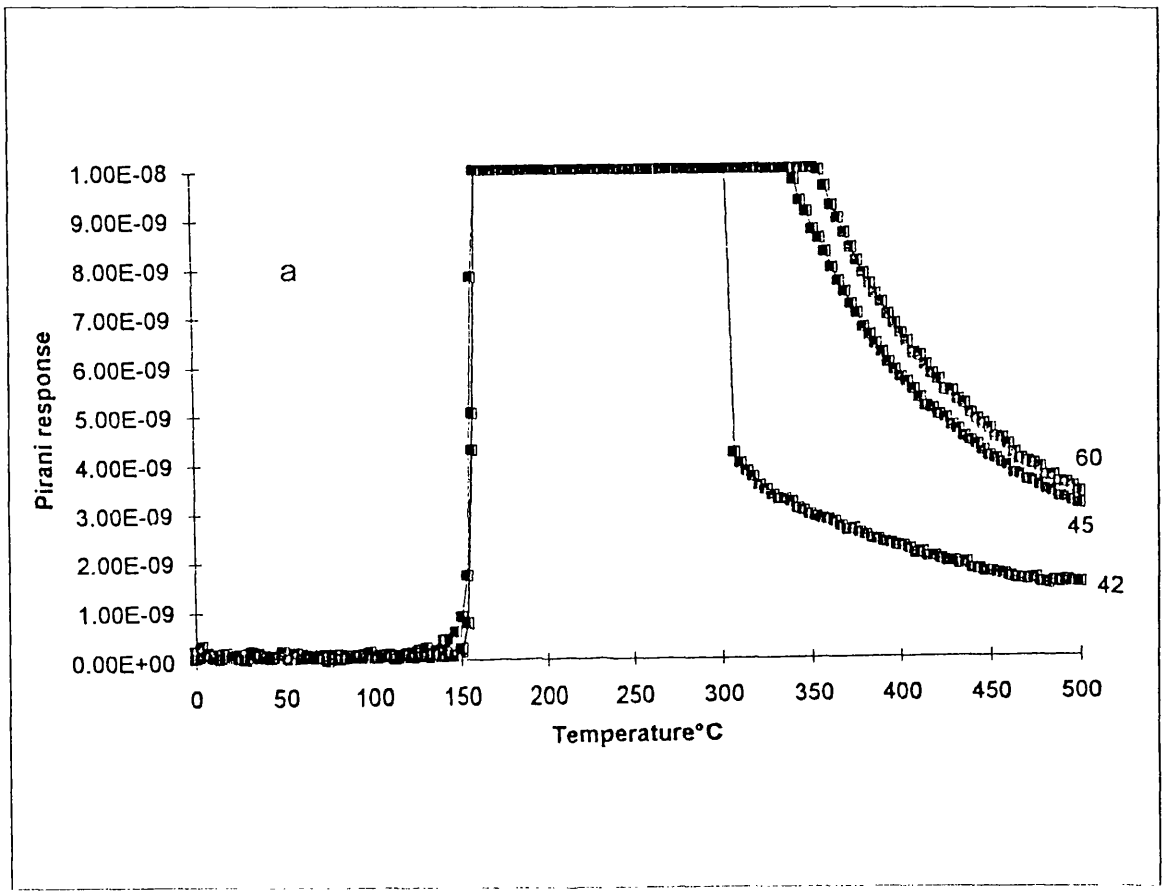


Fig. 8.4 The formation pattern of main degradation products of PIPAc (Heating rate 10°C/min up to 500°C) under TVA conditions

a: The formation of ketene through (m/e = 42) and acetic acid through (m/e = 60)

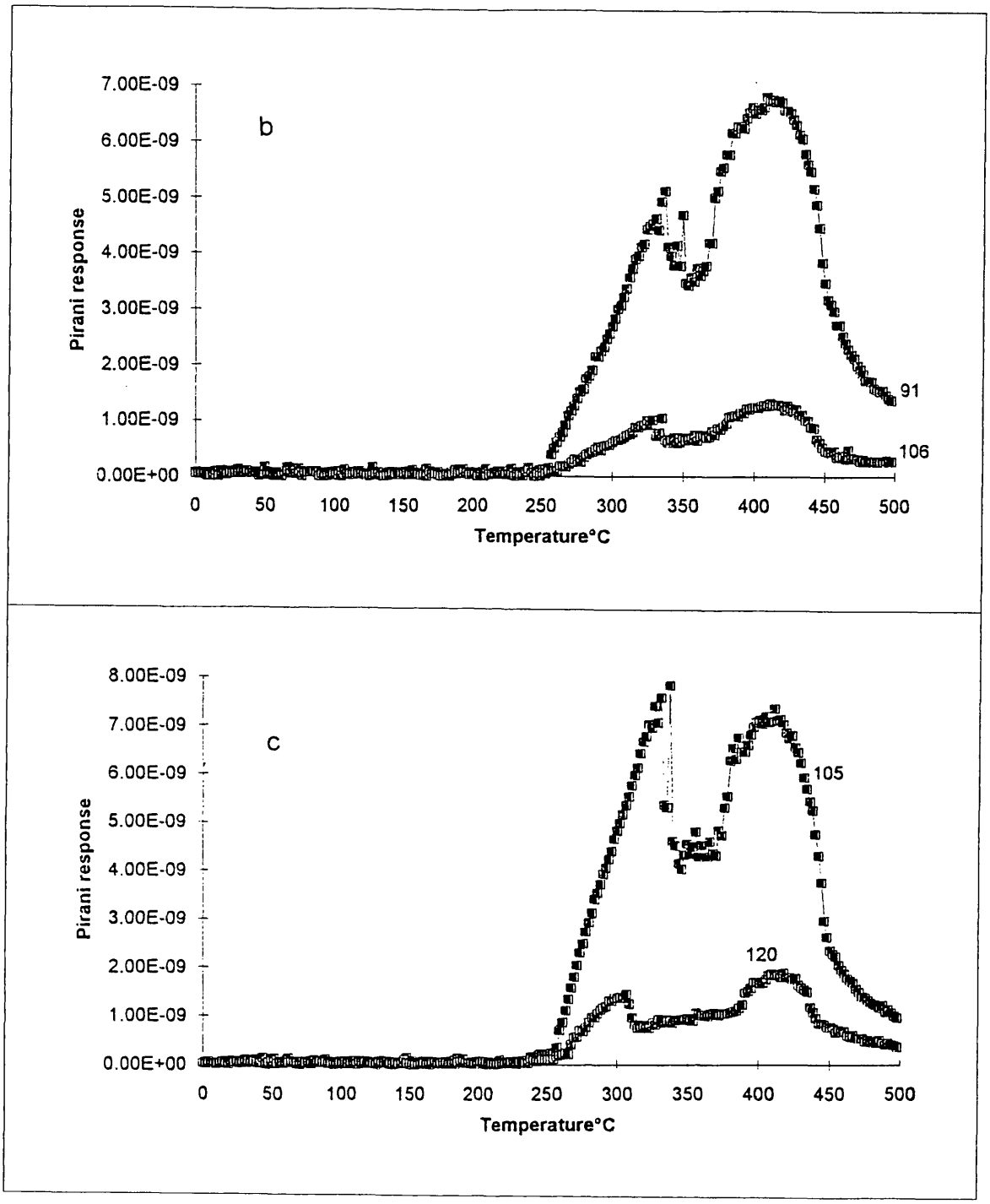


Fig. 8.4 Continued

b: Formation of *m*-xylene through (m/e = 91 and 106)

c: Formation of trimethyl benzene through (m/e = 105 and 120)

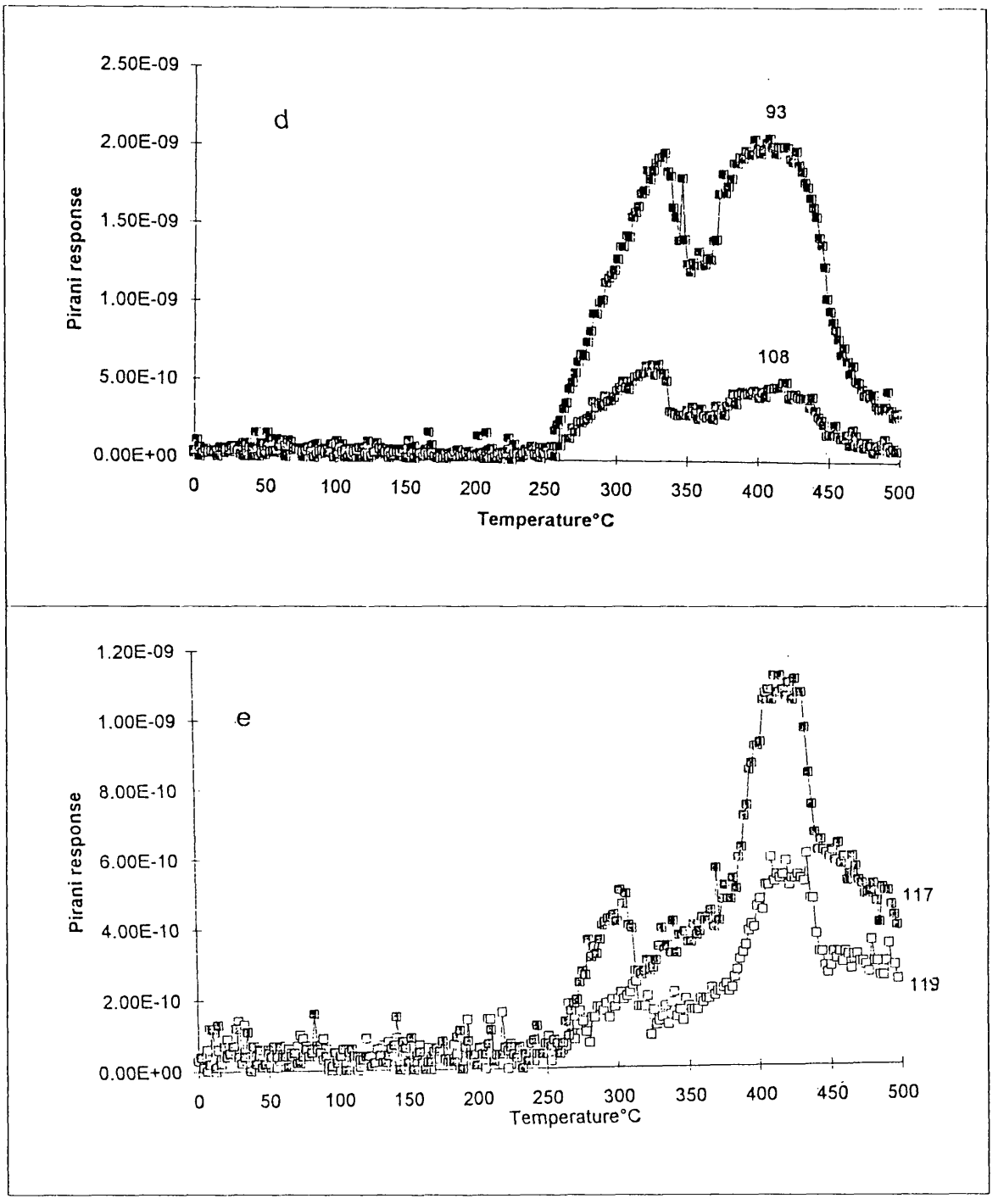


Fig. 8.4 Continued

d: Formation of 1,3-cyclopentadiene trimethyl (m/e = 93 and 108)

e: Formation of benzene 1-ehtenyl-2,4-dimethyl through (m/e = 117) and benzene 1-ehtyl-2,4-dimethyl through (m/e = 119)

Products like dimethylethylbenzene (MW = 134) and dimethylethenylbenzene (MW = 132) are shown by their characteristic ions (m/e = 117 and 119) are presented in Fig. 8.4d. The formation of product trimethyl 1,3-cyclopentadiene (m/e = 93 and 108) can be seen in Fig. 8.4e. All of these products are formed in two stages, to very low extent in the second stage (250-350°C) and to a higher extant in the third stage of decomposition (350-500°C).

The very small fraction of non-condensable gases is formed only in the third stage of degradation. The polymer steadily decomposes leaving less then 1% of residue (Table 8.2) in programmed heating up to 500°C under vacuum. The TG curve indicates a slightly greater amount of residue (3%) than observed in the TVA experiments. A possible reason could be the high vacuum (10^{-5} torr) in the TVA system which assists product volatilisation, while in the TG the nitrogen is a less efficient carrier.

SUBAMBIENT THERMAL VOLATILISATION ANALYSIS

The total condensable volatile pyrolysis products collected in a liquid nitrogen trap (- 196°C) after the TVA experiment were subjected to an initial separation by subambient thermal volatilisation analysis (SATVA).

The SATVA trace for poly(isopropenyl acetate) is presented in Fig. 8.5. Peak 1 is due to small fraction of carbon dioxide. Peaks 2 & 3 of very small magnitude are produced by ketene and isobutene, while peak 4 is mainly due to acetic acid and small amount of ketene. The material distilled at peak 5 is the liquid fraction. The liquid fraction was collected and analysed by IR spectroscopy and GC-MS.

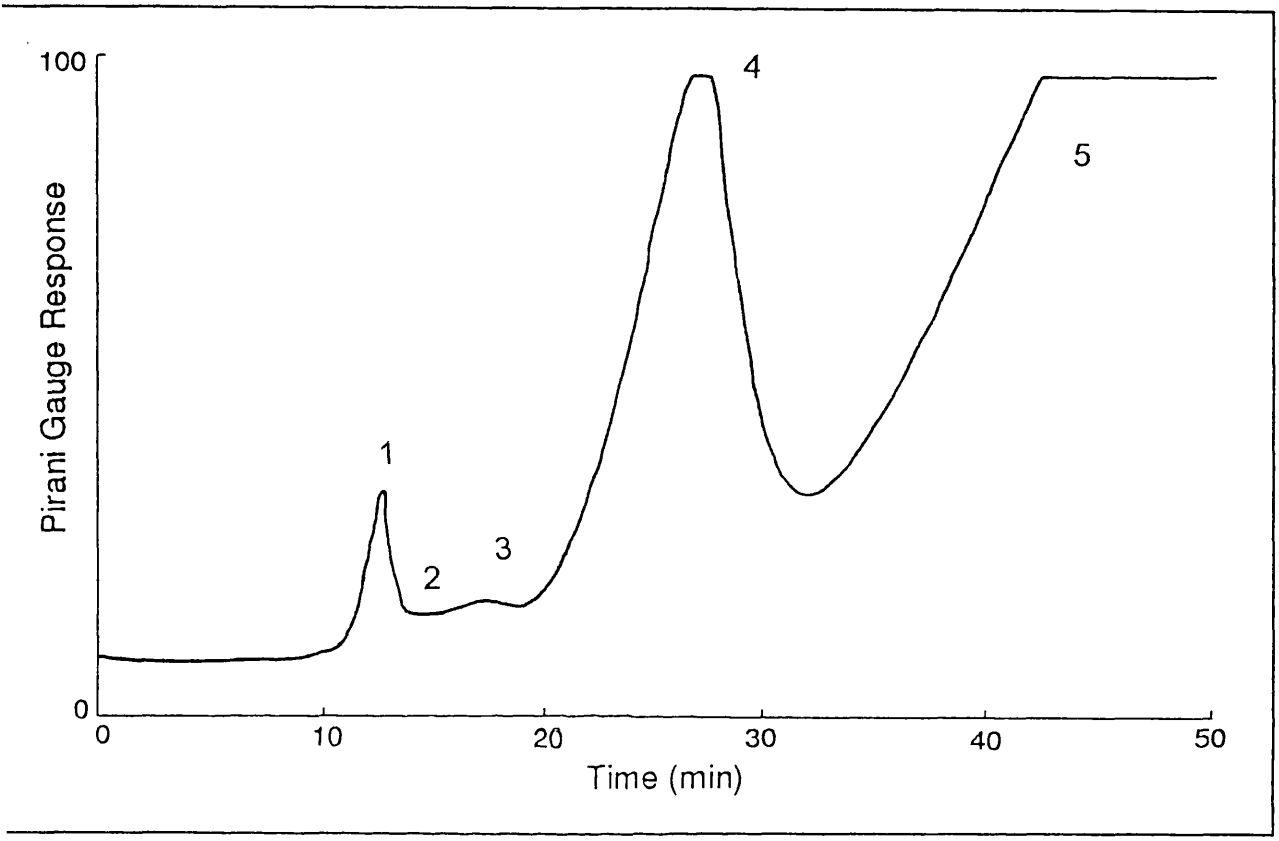


Fig. 8.5 SATVA curve for separation of the condensable volatile degradation products from degradation under TVA conditions to 500°C of the PIPAc.

COLD RING FRACTION

The cold ring fraction (CRF) consisted of light yellow products which were condensed on upper part of the degradation tube, from where it was removed using a volatile solvent and transferred to a weighed glass sample tube. After evaporation of the solvent at room temperature, the weight of the cold ring fraction was determined. This fraction was examined by IR spectroscopy and mass spectrometry using a probe heated to different temperatures.

The IR spectrum of the CRF is compared in (Fig. 8.6b) with the spectrum of undegraded polymer (Fig. 8.6a). The IR spectrum shows a high aliphatic content (2949-2860, 1450, 1375 cm^{-1}). The (νC=O) absorption at 1740 cm^{-1} (ν_aC—O—C) at 1248 cm^{-1} and (ν_sC—O—C) at 1170 cm^{-1} and νO R (where R is the polymer back bone) at 1020 cm^{-1} show the presence of some ester groups in the tar. These ester groups are probably carried into the tar fraction by breakdown products formed in the second stage of decomposition above 250°C.

The IR spectrum shows a heavy aromatic content (3030, 1600, and 1450 cm^{-1}). In the fingerprint region there is the out of plane bending of 5 and 4 H atoms (740 cm^{-1}), 3 (810 cm^{-1}), 2 (850 cm^{-1}) and 1 (894 cm^{-1}) H atoms. These vibrations together with the in plane bending vibrations in the region 960-1200 cm^{-1} suggest aromatic rings with variable degree of substitution. There is a small absorption at 1650 cm^{-1} attributable to conjugated double bonds, although such a band is also present in condensed ring aromatic hydrocarbons. The IR spectrum of the CRF resembles very much that of the polymer degraded to (320-360°C) Fig. 8.8(e-f).

Table 8.3. Assignment of the major peaks in the IR spectrum of undegraded PIPAc.

Band (cm^{-1})	**Assignment**
2990	CH_3 asymmetric stretch
2940	CH_2 asymmetric stretch
2855	CH_3 symmetric stretch
1735	C=O stretch of ester group
1460	CH_2 bending deformation
1435	CH_3 asymmetric bending
1370	CH_3 symmetric bending
1248	(C—O—C) symmetric stretching
1130	(C—O—C) symmetric stretching
1026	(CH—O) symmetric stretching
950	(C—CH_3) rocking
800, 605	(O—CO) Bending and other deformations

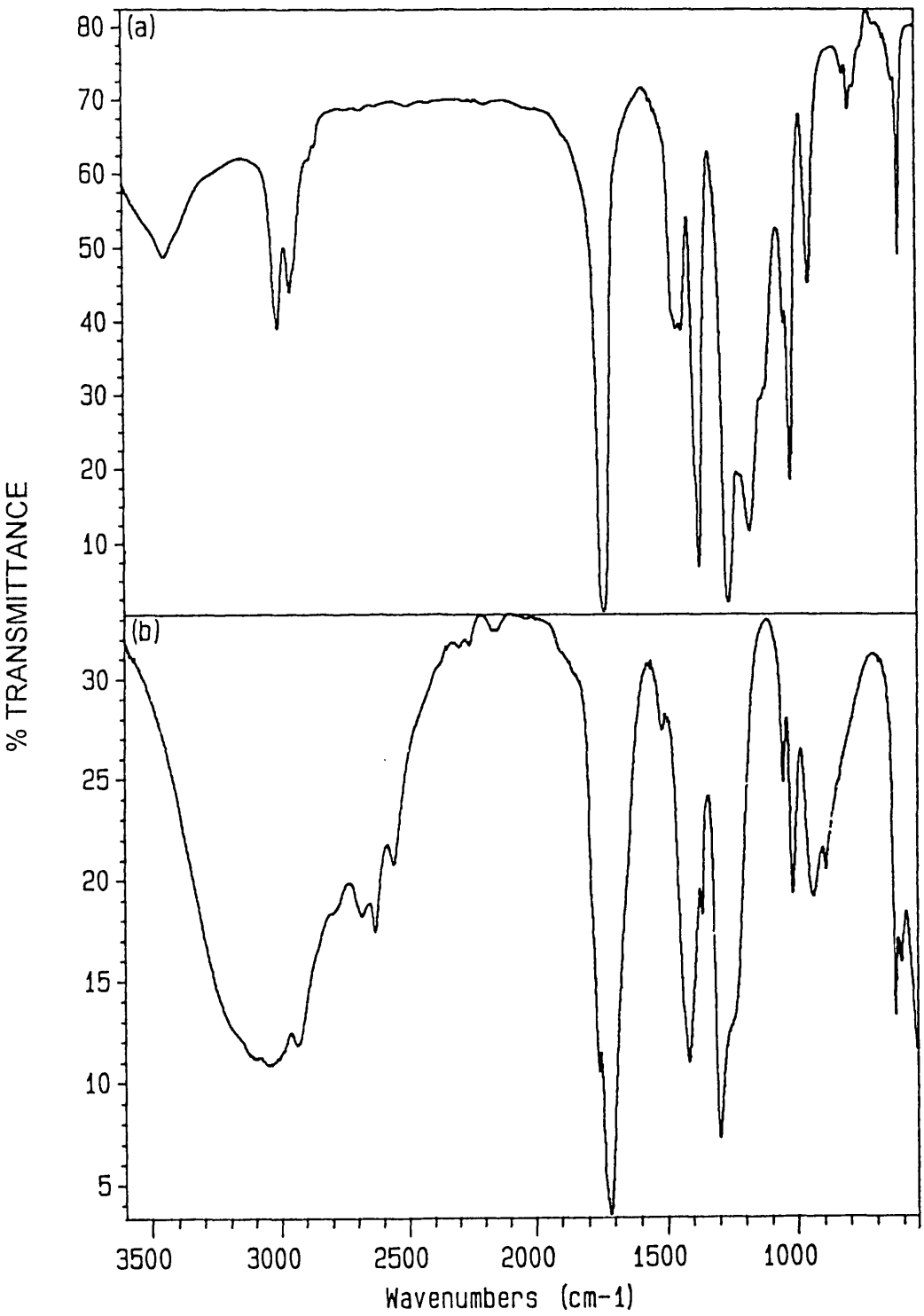


Fig. 8.6 IR spectra of (a) undegraded copolymer (b) cold ring fraction from PIPAc degraded to 500°C under TVA conditions.

CONDENSABLE PRODUCTS

a. LIQUID FRACTION

In the TVA experiment carried out under vacuum, the gas and liquid fraction condensed in a liquid nitrogen trap was subsequently distilled and weighed, (Table 8.2). The collected liquid fraction was further analysed by IR spectroscopy and GC-MS technique. The IR spectrum of the liquid fraction is presented in Fig. 8.7. The spectrum shows the presence of a high content of acetic acid (1740, 1248 cm^{-1}), together with aromatic hydrocarbons and some unsaturation (C=C) at 1650 cm^{-1}. The products of the liquid fraction analysed by GC-MS are listed according to their relative abundance in Table 8.4.

b. GASES

The condensable gaseous products separated as a result of a SATVA experiment were examined by IR spectroscopy and mass spectrometry. The latter studies were carried out during SATVA separation with an on-line quadrupole mass spectrometer as the gaseous products warmed up from the liquid nitrogen trap to room temperature. The gaseous products were also examined by IR spectroscopy, after collecting them in gas cells during the SATVA separation. The gaseous products identified were mainly ketene, carbon dioxide isobutene and ethene.

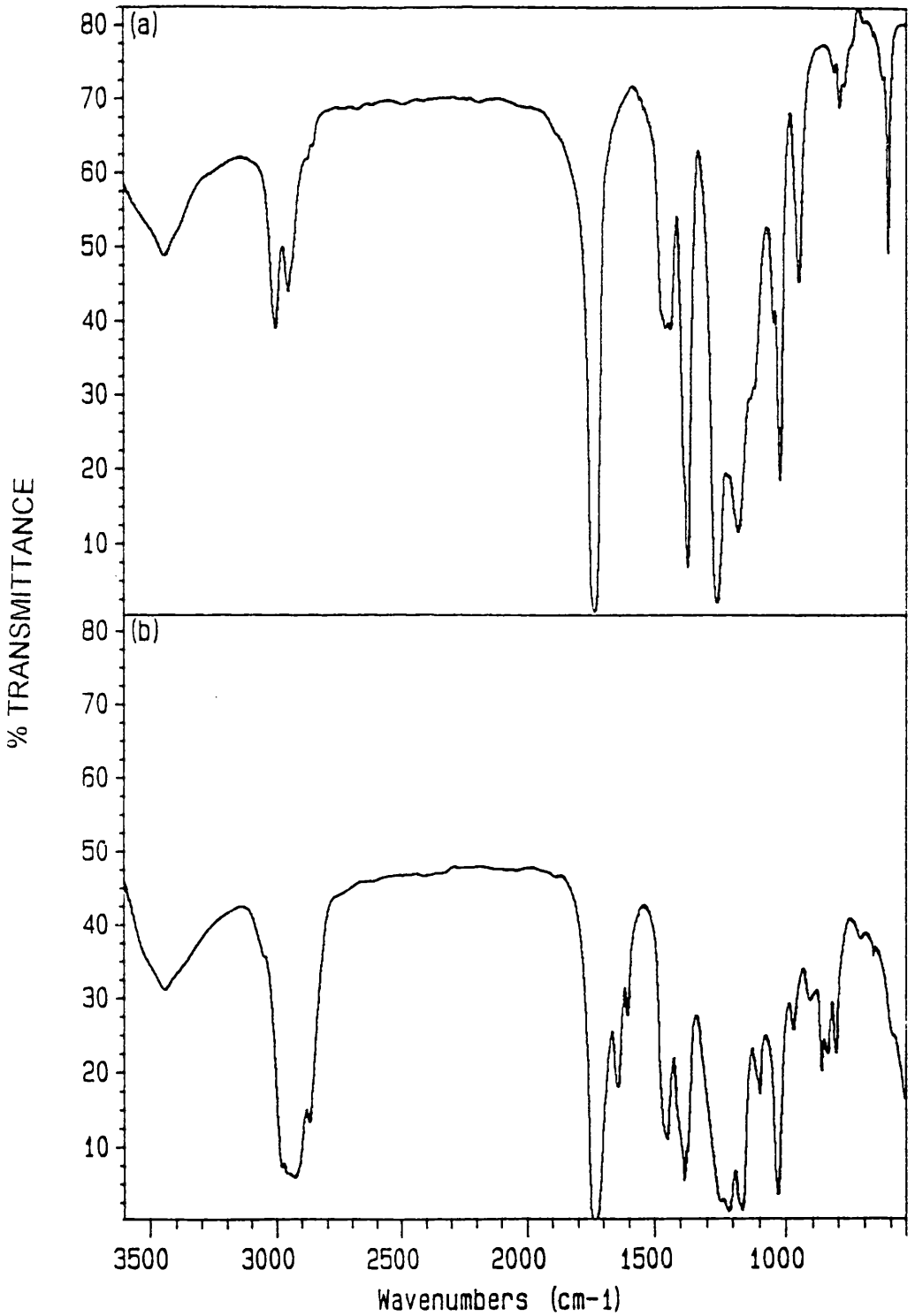


Fig. 8.7 Infrared spectra of the condensable gases and liquid fraction for degradation of PIPAc to 500°C under TVA conditions.

Table 8.4. Liquid fraction collected after pyrolysis of PIPAc analysed by GC-MS. The products are listed according to relative abundance

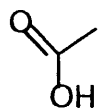
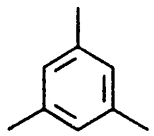
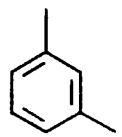
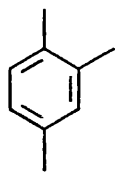
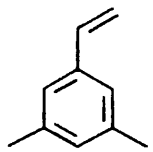
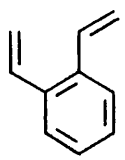
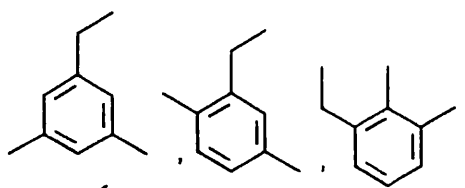
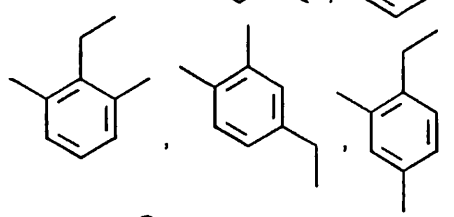
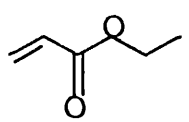
	Products	MW
1		60
2		120
3		106
4		120
5		132
6		162
7	 	134
8		100

Table 8.4 (continued)

	Products	MW
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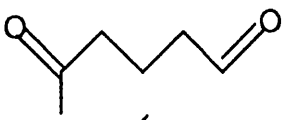
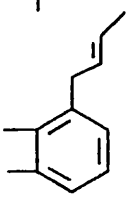
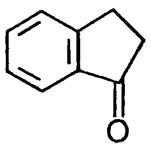
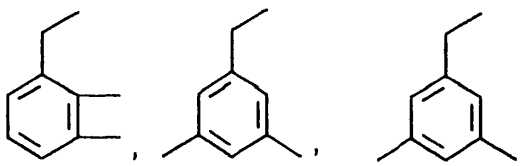
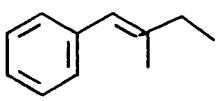
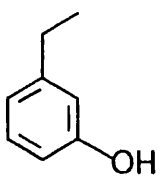
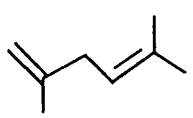
10		142
11		160
12		146
13		134
14		146
15		122
16		90

FTIR STUDIES OF THE STRUCTURAL CHANGES IN THE POLYMER DURING DEGRADATION

The transformations in the structure of poly(isopropenyl acetate) with temperature were followed by heating a 10 mg portion of film cast uniformly on a stainless steel plate from a solution in tetrahydrofuran (THF). The cast film was evacuated in a vacuum oven at 40°C for 24 hours. The film was then finally heated at 80°C for 30 min to eliminate any trace of THF remaining.

The polymer film was heated at a rate of 10°C/min to a chosen temperature in the range of 160-440°C in vacuum. The film was then cooled to room temperature and examined by reflection absorption FTIR spectroscopy. In some cases the spectra were subjected to automatic deconvolution, a processing mode in the existing software.

The structural changes in the polymer upon heating to 160, 240, 280, 320, 360, 400 and 440°C are illustrated in Fig. 8.8(b-h). The main absorption bands of the undegraded polymer (Fig. 8.8a) are summarised in Table 8.3.

Heating PIPAc to 160°C results in loss of acetate groups and the formation of conjugated double bonds in the polymer backbone. This transformation is indicated by the appearance of the 1650 cm^{-1} band (Fig. 8.8b). At 240°C many ester groups are lost : the ν_a C—H of CH_3 groups linked to O (2997 cm^{-1}) is substituted by ν_a C—H of CH_3 linked to C (2980 cm^{-1}). This is due to the fact that many CH_3O— groups as part of the ester function disappear and the vibrations characteristic of CH_3 groups become more evident. The symmetric C—O—C stretching at 1170 cm^{-1} has almost disappeared. A largely conjugated system is formed (3075, 1650 cm^{-1}). The concentration of CH_2 groups has also decreased significantly since its bending vibration at

1460 cm^{-1} cannot be seen any more. Aromatic rings are also present in the polymer as shown by the newly appeared bands at 1620, 1450, 890 $cm.^{-1}$ The presence of the 1620 cm^{-1} absorption (shoulder) suggests condensed aromatic rings. A band at 1600 cm^{-1} would be expected for mononuclear rings. The increased absorption at 2866 cm^{-1} is also characteristic of C—H vibrations of condensed aromatic rings. It overlaps the symmetric stretching of CH_3 and CH_2 groups at the same position.

At 280°C the ester groups have considerably diminished, as shown by the reduced intensity of the characteristic vibrations. Aromatic rings condensed (1620 cm^{-1}) and non condensed (1600 cm^{-1}), and conjugated double bonds (1647, 3070 cm^{-1}) are all present. The aromatic rings are strongly substituted for only the out-of-plane bending of isolated C—H groups present at (890 cm^{-1}). The band at 890 cm^{-1} is also indicative for the chain end type of unsaturation.

At 320 and 360 °C transformations continue with even more pronounced loss of acetate groups, extended aromatisation and conjugated double bond formation. At 360°C some ester groups still survive, but at 400°C they have disappeared completely. The charred polymer at 400°C has an extended aromatic system, some CH_3 groups survive as substituents to aromatic rings. There are only very small out of plane bending vibrations due to H atoms attached to the aromatic rings present at this stage of degradation.

In order to provide clear evidence for the formation of unsaturation (double bonds) and aromatic rings, the spectra of thermally degraded polymer at various temperatures were subjected to automatic deconvolution. Fig. 8.9 presents the region of 3200-1500 cm^{-1} of the deconvoluted spectra. The appearance of the conjugated unsaturation indicated by the bands at 3070

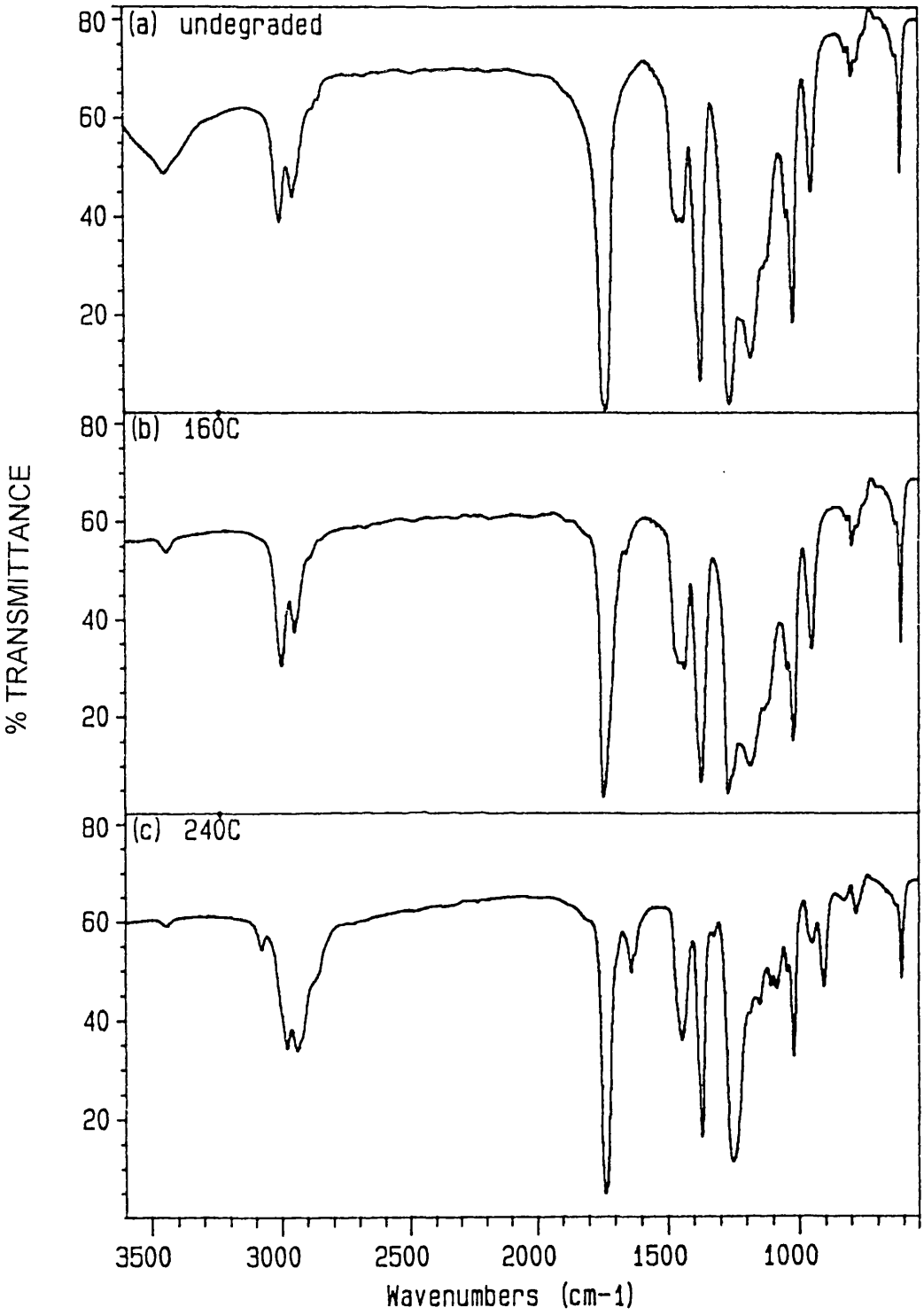


Fig. 8.8 Infrared spectra of PIPAc: (a) before and after heating in vacuum to: (b) 160°C (c) 240°C

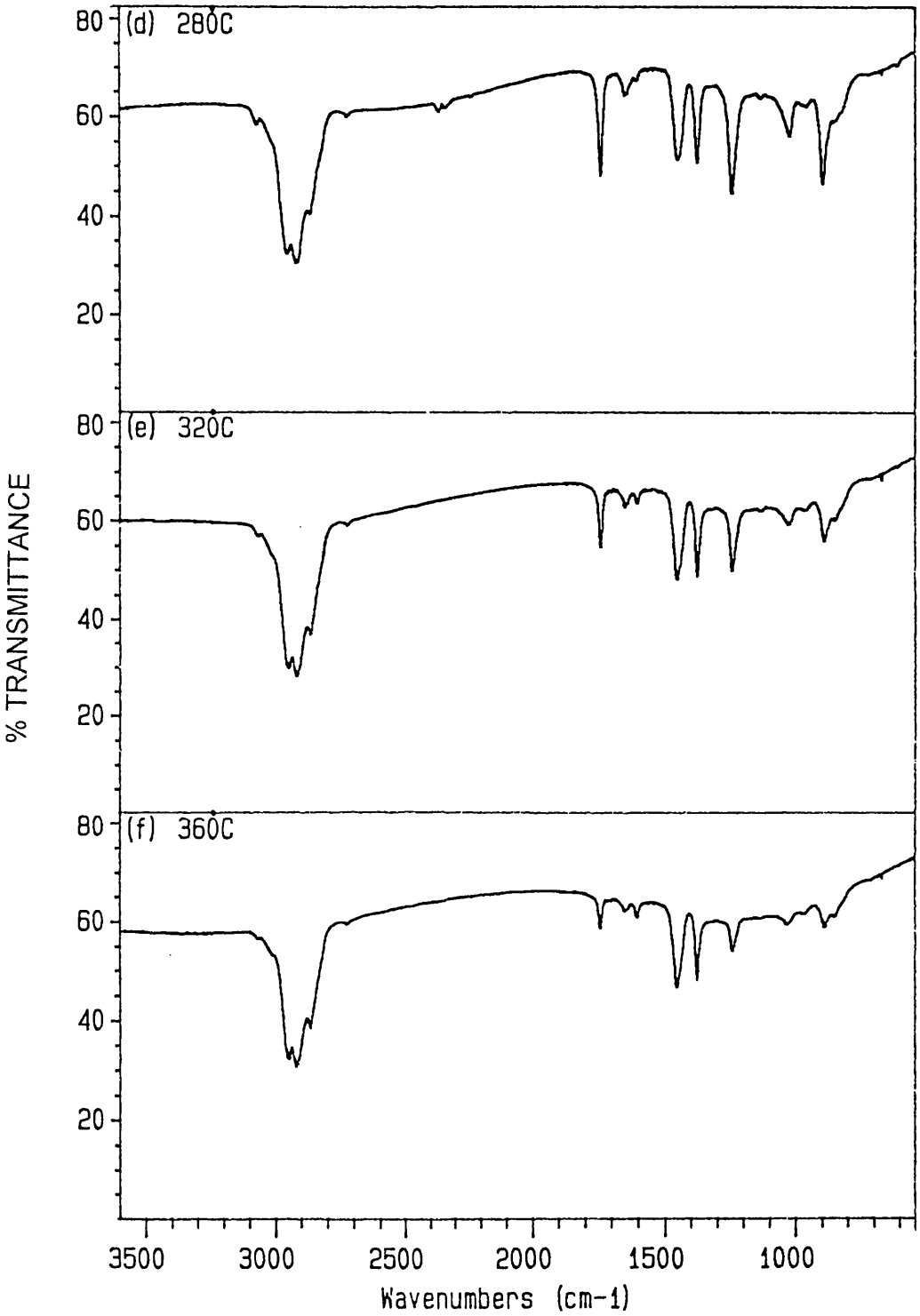


Fig. 8.8 Continued (d) 280°C (e) 320°C (f) 360°C.

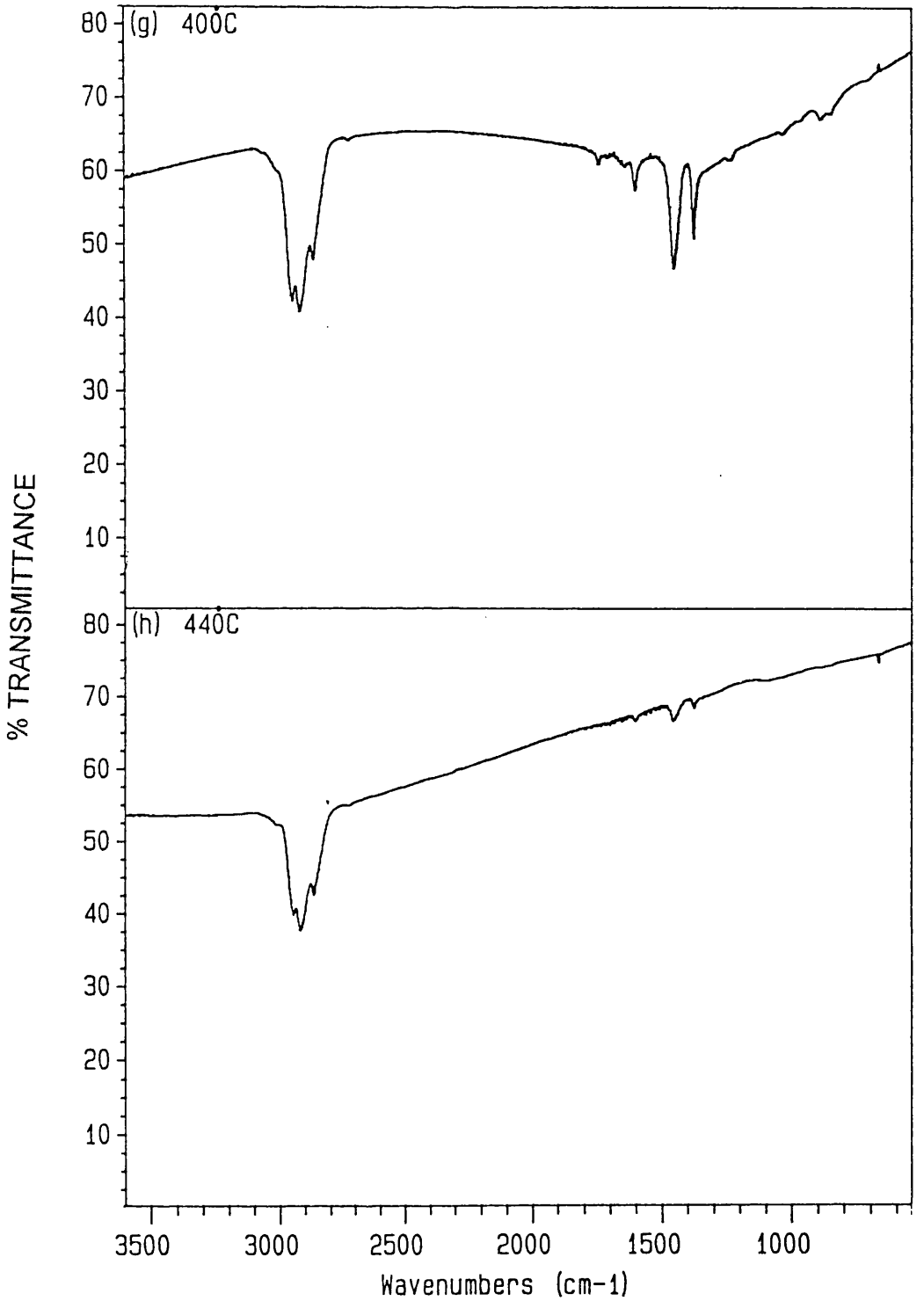


Fig. 8.8 Continued (g) 400°C (h) 440°C.

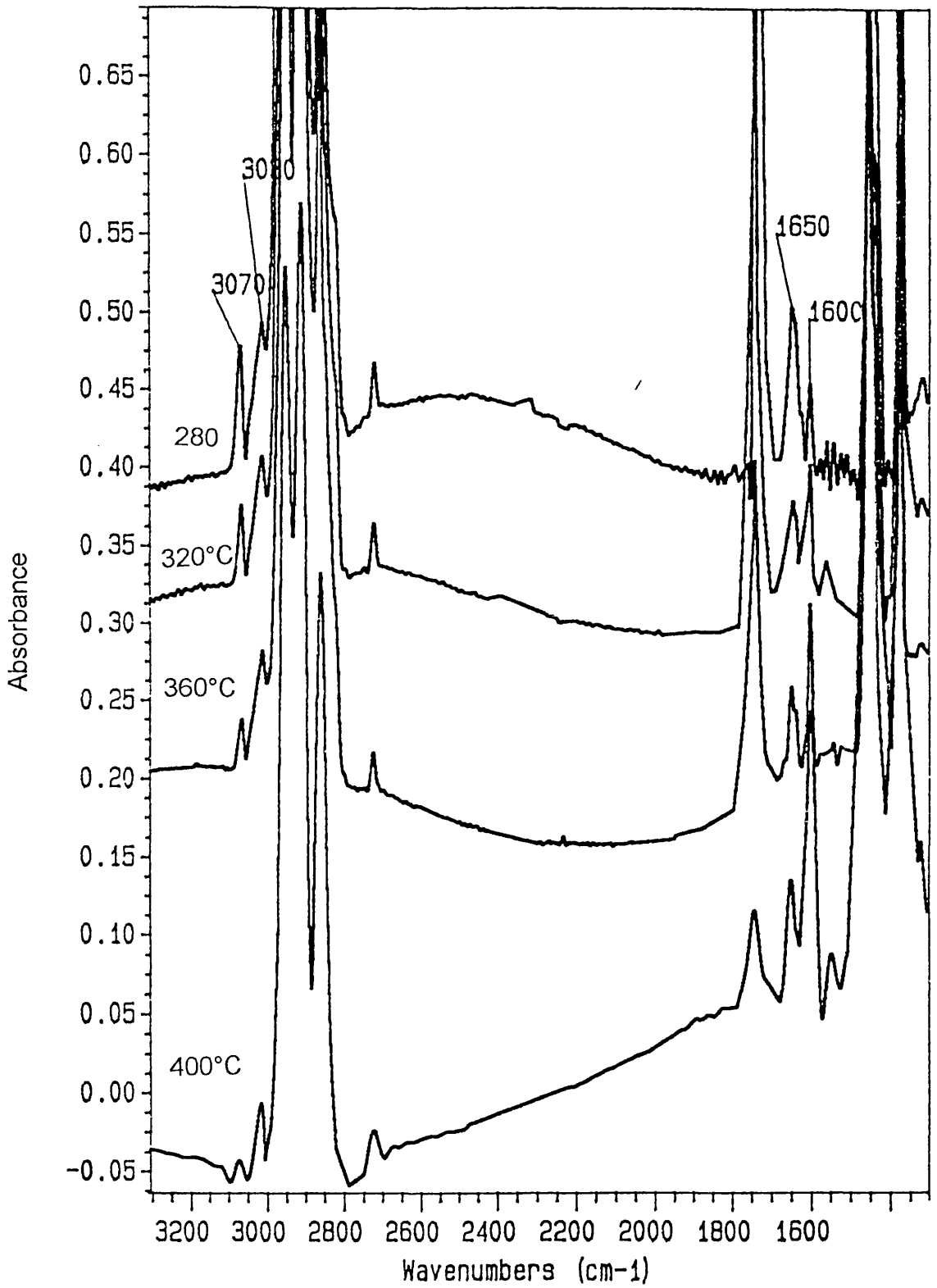


Fig. 8.9 FT-IR spectra of thermally degraded PIPAc obtained by deconvolution.

and 1650 cm^{-1} and the subsequent growth of the aromatic ring absorption (3030, 1600 cm^{-1}) at the expense of unsaturation can be followed in Fig. 8.9, through the continuous increase of the ratio between the intensities of the bands 3030/3070 and 1600/1650 $cm.^{-1}$

DISCUSSION

It is clear from the above presented results that the thermal degradation stages of PIPAc involve different mechanisms and yield different products. During the first stage (160-250°C) the major product formed is acetic acid. Other products are ketene, CO_2, and very small amount of aliphatic hydrocarbons (ethane, ethene).

PIPAc is closely related structurally to PVA. The difference between them is that the PVA has the major part of its acetate groups attached to secondary carbon atoms and only a small fraction of the acetate groups are attached to tertiary C atoms. The latter structure occurs at branching points and PVA is known to have an important fraction of branches (10 - 20 per 100 VA groups) (70,93). It is also considered that initiation in PVA thermal degradation is through the thermal dissociation of the acetate groups attached to quaternary carbon atoms at a branching point (70), although definite proofs are still lacking. In PIPAc all the acetate groups linked to tertiary C atoms. It is considered that initiation of thermal dissociation in PIPAc takes place through the acetate groups are attached to tertiary C atoms. Indeed all our results show that massive acetic acid elimination occurs in PIPAc between 160-250°C, while in PVA although a few acetate are lost at 160°C, the massive elimination takes place between 250 and 375°C. For both polymers the weight loss in the temperature interval corresponding to the first stage recorded by the TG curves suggests total loss of acetate groups. Both polymers show deep endotherms in their DSC thermogram associated with the loss of acetic acid. Scheme 1 presents the thermal degradation of

PIPAc. Reaction (1) shows the thermal dispersion of the acetate groups generating macromolecular radical (I) and acetate radicals. The acetate radicals are very active in H abstraction (reaction 2) at the methylene group generating radical (II) which reorganises with the expulsion of an acetate group and the formation of a double bond (reaction 3).

The attack of acetate radicals on CH_2 groups can continue as in reaction (4) and results in the formation of conjugated double bonds (reaction 5). Reactions (2) - (5) constitute the zip deacetylation of PIPAc which we believe to takes place through free radical mechanism. This view is supported by the formation of ketene simultaneously with acetic acid as shown by their ion monitoring (Fig. 8.4a). The ketene can be formed at this temperature only by the decomposition of the acetate radicals (reaction 6). The formation of ketene by decomposition of the acetic acid (reaction 7) is known to occur only at high temperature, above 350°C (27). A small amount of CO_2 has been observed which is also consistent with the decomposition of the acetate radical (reaction 8). The small amount of aliphatic hydrocarbons which has been observed can result from reaction of the CH_3 radical formed in reaction (8)

The tertiary radical (I) and to a smaller extent the secondary radical (II) can suffer chain scission. This is represented for radical (I) by reaction (9) which creates a macromolecule with terminal unsaturation and a macroradical (III) which is quite stable and likely to react by H abstraction. At higher temperatures the frequency of scission increases and by 500°C the polymer has decomposed leaving almost no residue. Another feature which distinguishes PIPAc from PVA is that in the latter reaction (9) is of less importance due to the fact that tertiary radicals are formed only at branching points. PVA produces sequences of up to 6 double bonds. There is crosslinking initiated by the double bonds, and aromatic hydrocarbon formation. As a result of crosslinking tendency and of aromatic rings

formation within the polymer, PVA produces an important fraction of residue (8%). In contrast, the concentration of radical (I) is high in PIPAc which increases the tendency for scission. As a result, PIPAc generates an insignificant fraction of residue.

The degradation stage between 250 and 350°C cannot be seen in the TG curve which shows only a steady weight loss of 10%. It can be seen as a shoulder in the TVA diagram, especially trace 1 corresponding to acetic acid and trace 2 corresponding to acetic acid and aromatic hydrocarbons. Indeed the continuous monitoring of specific ions show the formation of trimethyl 1,3-cyclopentadiene (Fig. 8.4d), *m*-xylene (Fig. 8.4b), trimethylbenzene Fig. 8.4c) and 1-ethyl-2,4-dimethyl benzene plus C4 alkylbenzene (Fig. 8.4e) in this temperature stage. Their formation is associated with a shallow endotherm in the DSC diagram (Fig. 8.2).

The third stage, between 350 and 475°C is very distinct on all the traces except for DSC where elimination of aromatic molecules is masked by the continuous decrease in the heat capacity due to the major changes in the polymer structure at higher temperature. The ion monitoring of the above hydrocarbons shows that they are mainly formed in the temperature range 350-450°C. According to the data presented above, the main reaction in second interval is the formation of aromatic hydrocarbon from the chain ends of the split radicals. Also, in this temperature interval, Diels-Alder condensation of conjugated double bonds takes place to produce a six membered ring structure which will break away in the next temperature interval. However, the scission overcomes the crosslinking tendency.

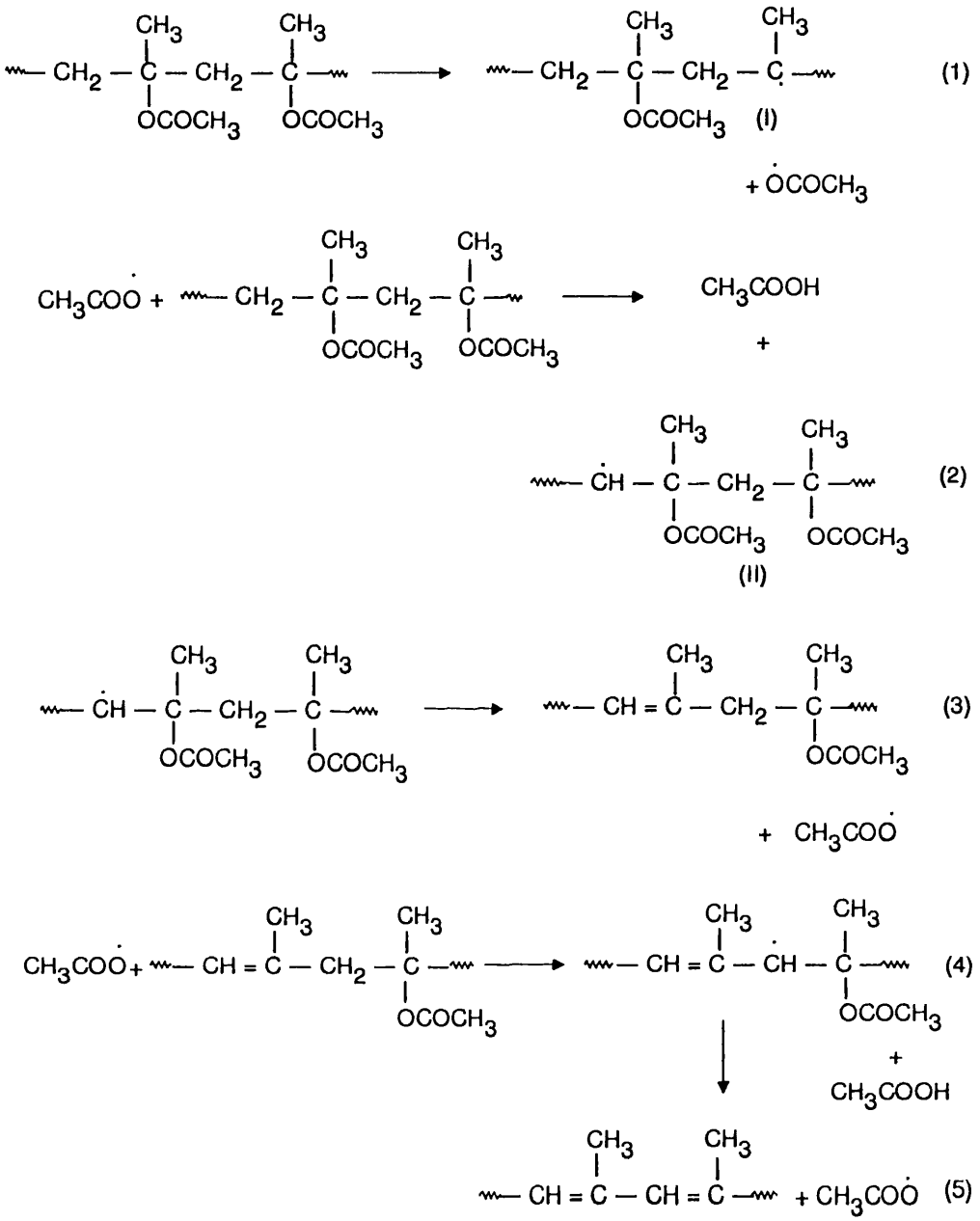
Scheme 2 presents the formation of aromatic hydrocarbon products present in liquid fraction. Double bonds appear as in reaction (10). A tertiary radical formed by the dissociation of an acetate group next to a double bond system will suffer scission as in reaction (11) generating radical (IV) which can

cyclise by the attack of the free radical on the double bond at the 6th C atom closing a ring as in reaction (12). The free radical (V) formed in reaction (12) generates 1,3,5-trimethylbenzene through scission followed by aromatisation. Other aromatic hydrocarbons can be formed through a similar mechanism. Table 8.4 shows the formation of oxygen-containing products such as ketones and alcohols. Their presence confirms the alkoxy radicals mechanism in the system. Through the breakdown of the O—CO link at higher temperatures the ester link scission is presented in reaction (14), in which an alkoxy and an acetyl radical are formed. The alkoxy radical can form a ketone and a methyl radical as in reaction (15) or can form an alcohol through H atom abstraction as an reaction (16). The ketone and alcohol functions are then carried away in the reaction products formed as a result of main chain scission. The acetyl radical can further decompose forming CO and a methyl radical as in reaction (17). The formation of CO has been observed only at high temperatures in the second stage of degradation.

Scheme 3 presents the Diels-Alder condensation of the conjugated double bonds (reaction 18) which is believed to take place also in the second degradation stage. Reactions (19) and (20) show schematically the breakdown of the condensed polymer at quaternary and tertiary C atoms with the formation of aromatic hydrocarbons. The formation of aromatic hydrocarbons through this mechanism is in fact more complicated by severe sterochemical rules which governs Diels - Alder condensation and by the orbital symmetry rules which govern the aromatisation of substituted hydrocarbons. The presence of CH_3 substituents is another factor which differentiates PIPAc from PVA and which may restrict some Diels-Alder condensation and crosslinking and so facilitate scission.

Mechanism for thermal degradtion of PIPAc

Scheme 1



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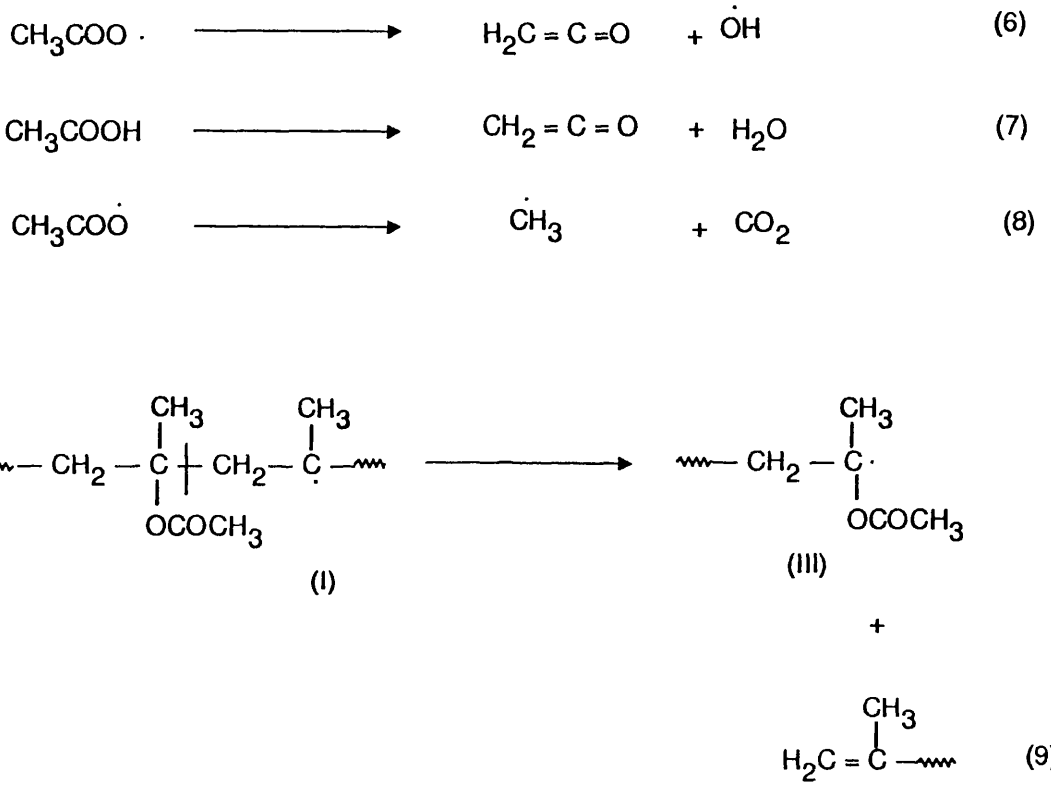
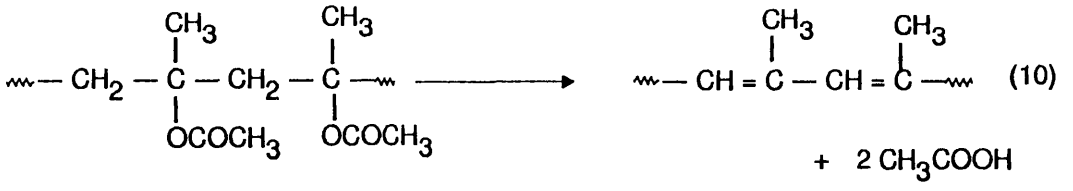
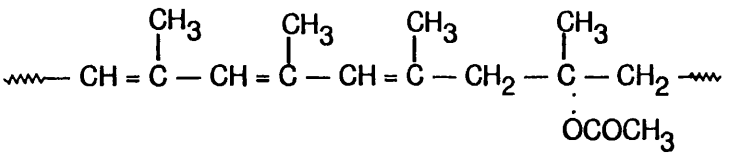
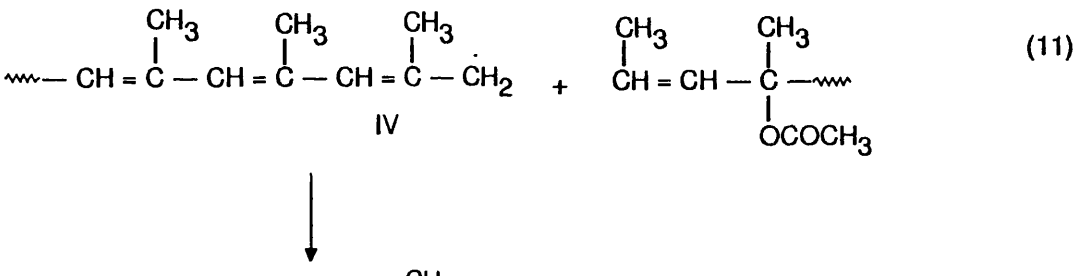


Scheme 2



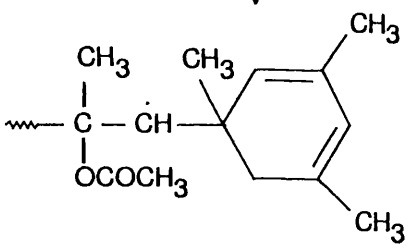
(10)





(11)

IV



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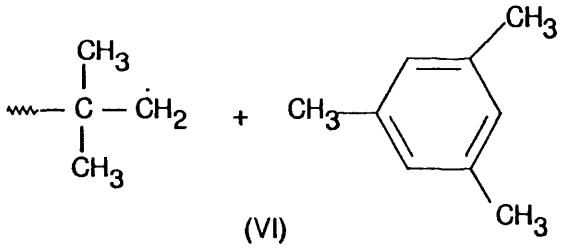
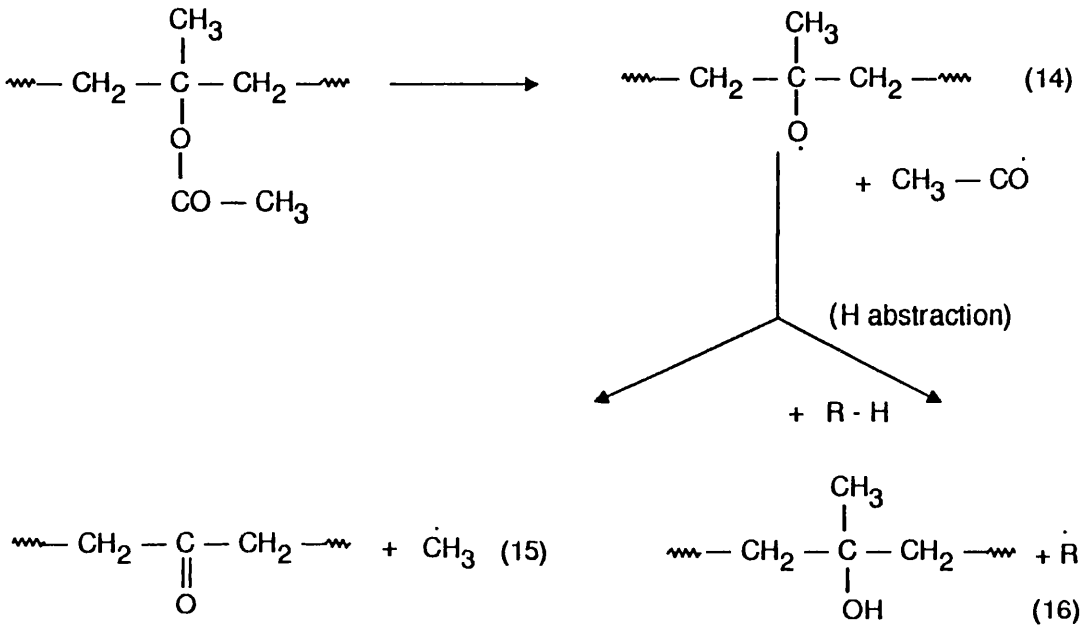
(V)



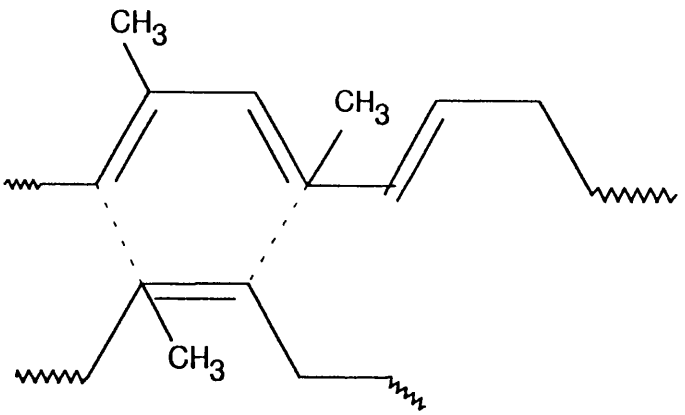
(13)

(VI)

Scheme 2 (continued)



Scheme 3



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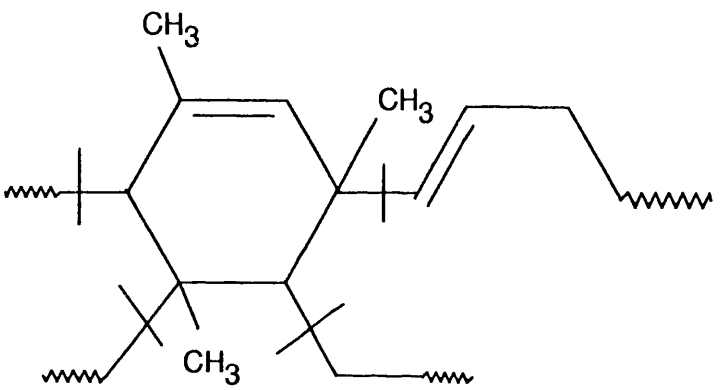

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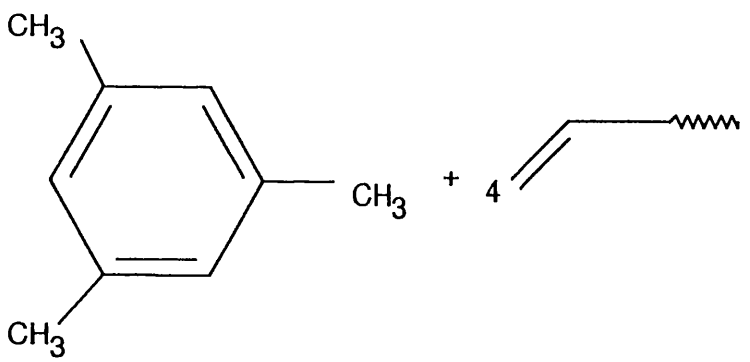


(20)

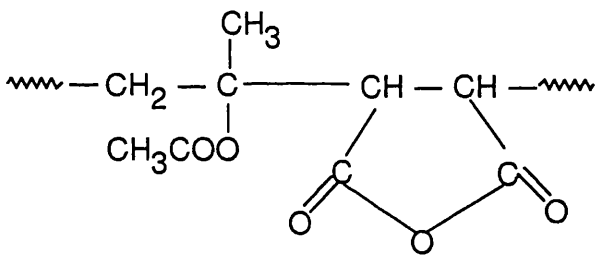
CHAPTER NINE

THERMAL DEGRADATION BEHAVIOUR OF AN ALTERNATING COPOLYMER OF MALEIC ANHYDRIDE - ISOPROPENYL ACETATE

INTRODUCTION

The polymerisation of alternating copolymers (94) and in particular of the copolymerisation of maleic anhydride and vinyl acetate have been studied in detail (94-98). The thermal degradation behaviour of these types of material have received very little study only in the recent years (33,82,86,99). The thermal degradation behaviour of alternating copolymer of maleic anhydride with isopropenyl acetate (MAn—IPAc) has never been studied before.

The MAn—IPAc copolymer was prepared by free radical polymerisation using AIBN as initiator. The polymerisation method is described in Chapter 2 while the preparation conditions are listed in Table 9.1.



Most of the thermal degradation studies have been carried out by heating the polymer in nitrogen atmosphere or under vacuum conditions. The structural changes in the copolymer during degradation at various temperatures up to 440°C have been investigated by IR spectroscopy.

Table 9.1. The preparation conditions for the alternating copolymer of MAn—IPAc copolymer by free radical polymerisation.

Amount of isopropenyl acetate	15 ml (0.14 mole)
Amount of maleic anhydride	13.6 gram (0.14 mole)
Amount of initiator	0.1 % *
Time of polymerisation	8 hours
Temperature of polymerisation	60°C
Conversion	19.29 %

* Relative to the total weight of monomers

Isothermal studies were also carried out at lower temperatures for various lengths of times under vacuum conditions. The product fractions collected during the thermal degradation up to 500°C (non-condensable, condensable volatile products and residue) were analysed by specific means.

THERMOGRAVIMETRY (TG)

The thermogravimetric (TG) and differential thermogravimetric (DTG) curves for MAn—IPAc copolymer under dynamic nitrogen atmosphere at a heating rate of 10°C/min up to 500°C are shown in Fig. 9.1. They indicate two stages of polymer thermal breakdown. An initial weight loss of 32% is observed in the temperature region 150 to 250°C, with rate maximum at 220°C. This weight loss in the first stage corresponds to total loss of acetic acid by the polymer. The IR spectrum of the partially-degraded polymer shows the almost complete disappearance of ester groups at 240°C (Fig. 9.8c). Further rapid weight loss of 34% is observed in the temperature region 250-350°C. This rapid weight loss is possibly due to the breakdown of anhydride rings.

Above 350°C and up to 500°C a slow and steady weight loss of 18% is observed, which indicates that some stable material is decomposing gradually.

There is a considerable amount of residue (15%) for the MAn—IPAc copolymer after heating to 500°C.

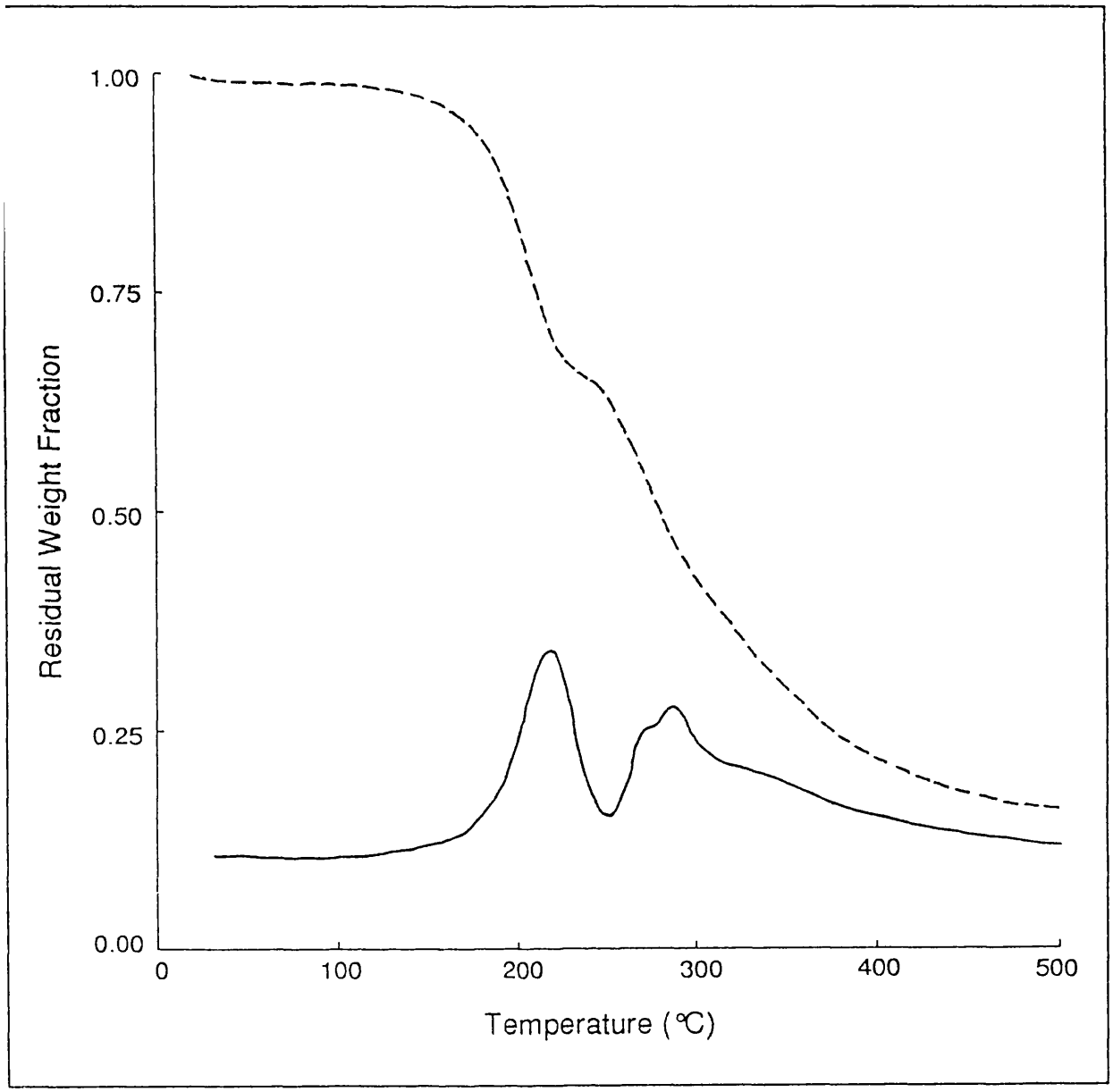


Fig. 9.1 TG and DTG curves obtained for MAn—IPAc copolymer (heating rate 10°C/min, nitrogen flow)

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The thermal stability of the alternating copolymer of maleic anhydride-isopropenyl acetate has also been investigated by DSC under dynamic nitrogen at a heating rate of 10°C/min up to 500°C.

The DSC curve is presented in Fig. 9.2. It shows a large endotherm in the temperature region of 150 to 260°C with the thermal effect of 200J/g. This endotherm corresponds to the weight loss of 32% observed in the first stage of decomposition indicated in the TG curve (Fig. 9.1). The DSC curve presents a very small endotherm between 260 to 300°C with an enthalpy change of 13.85J/g. This endotherm corresponds to the weight loss indicated by the TG curve between 250 and 350°C. Above 300°C the DSC curve does not reflect any more the latter stage of degradation. The heat capacity of the sample decreases continuously in this temperature region due to changes in polymer structure.

THERMAL VOLATILISATION ANALYSIS

The MAn—IPAc copolymer was examined as a 50 mg powder sample in the TVA system under vacuum using programmed heating at a rate of 10°C/min to 500°C. The TVA trace presented in Fig. 9.3 shows the two main stages of degradation. The first between 150 and 250°C with rate maximum at 205°C and the second between 250 and 500°C. The product of first stage is entirely acetic acid which escapes the traps at 0 and -45° (traces 1 and 2). Acetic acid can give rise to a limiting rate effect in the -45° trace if the sample size is sufficiently large (39) which manifests itself if volatile products continue to escape the trap at -45°. In fact it is the acetic acid condensed here which slowly distils to the main liquid N_2 traps.

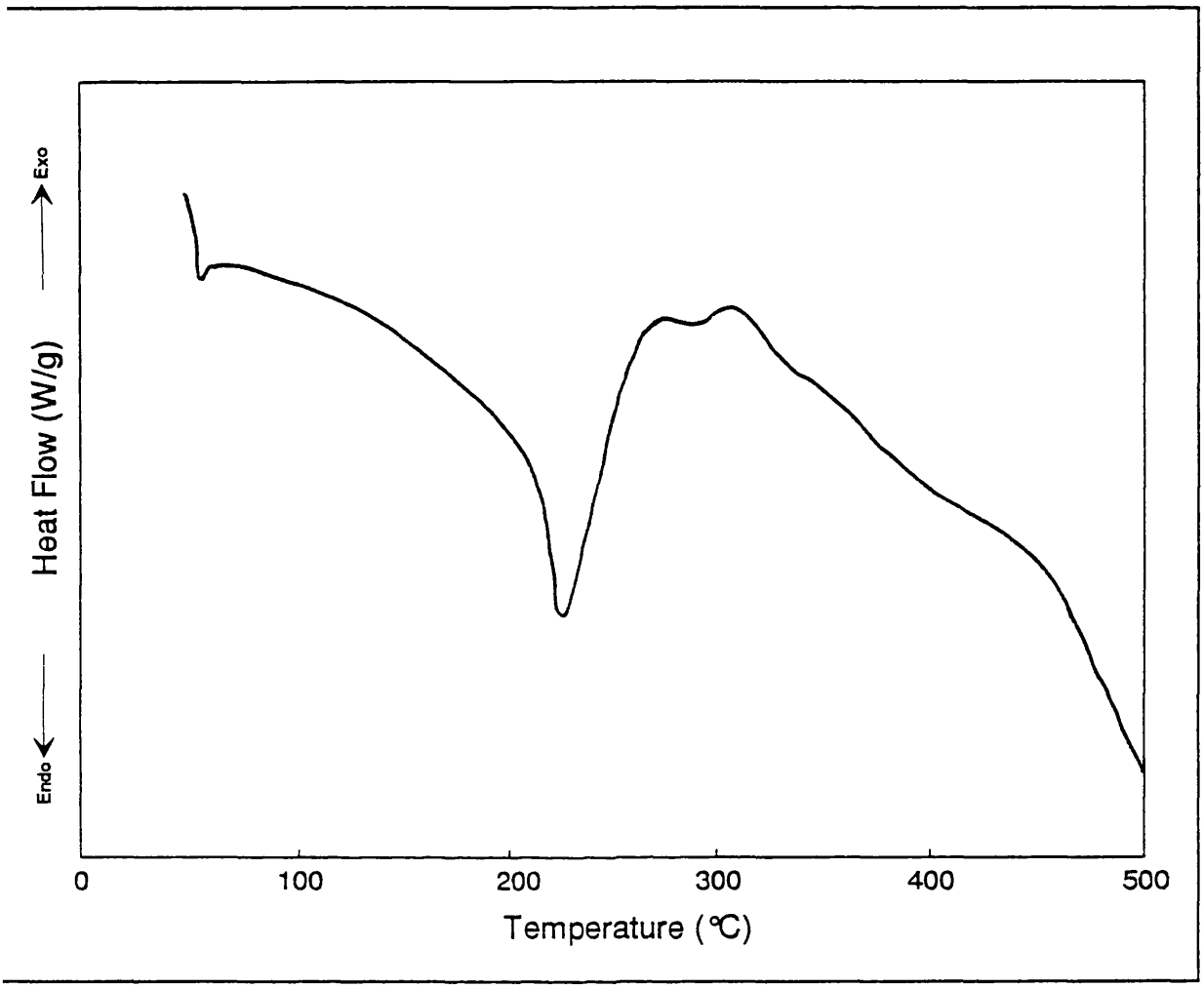


Fig. 9.2 DSC curve for MAn—IPAc copolymer (heating rate 10°C/min under nitrogen flow).

The result is that the -45° trace in Fig 9. 3 is placed above the 0° trace in the second stage of degradation.

For decomposition in between 250°C and 500°C it can be seen from the TVA curve that there are two rate maxima. The first, is very sharp and occurs just after the end of the first stage at 270°C. This rate maximum is also observed in the TG curve. The second occurs is towards the end of the second stage at 460°C.

It is obvious from the TVA trace that the products evolved in the second stage of degradation are of higher volatility and non-condensable at all temperatures (0 to -196°C). Above 250°C, the higher Pirani response after the -100° trap suggests a large fraction of CO_2 escaping the trap. The presence of CO_2 above this temperature indicates the breakdown of anhydride rings which are presumably stable up to 250°C. The Pirani response after the -75° trap is due to ketene and other compounds of low boiling points. The non-condensables (mainly carbon monoxide together with small amount of methane and hydrogen) escape the -196° trap.

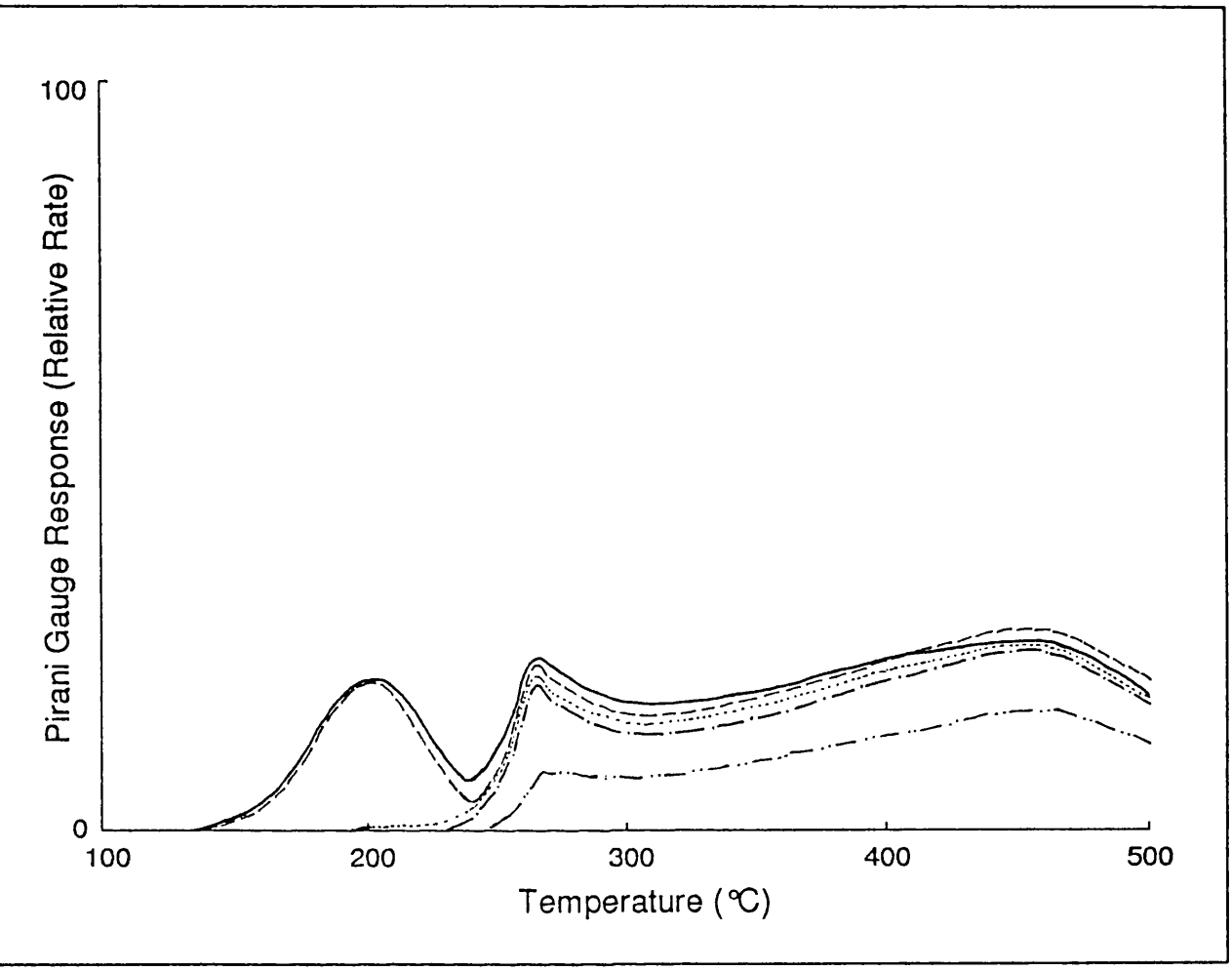
At the end of the TVA experiment the condensed fractions of different volatility produced by pyrolysis were quantitatively determined by direct weighing and are presented in Table 9.2. The major fraction is the cold ring fraction (37%) followed by condensable gases and liquids (34.50%), noncondensable gases (15.5%) and residue (13%). The residue indicated in TG curve is around (16%). A possible reason for this small difference has already been explained in an earlier Chapter 8.

During the MAn—IPAc copolymer degradation in vacuum up to 500°C in the TVA system monitoring by mass spectroscopy of the formation of main degradation products has been carried out. Fig. 9.4 (a-g) shows the evolution of individual volatile products with temperature which

was followed by plotting the intensity of their characteristic ions recorded by mass spectrometry versus time (temperature). The evolution of acetic acid was followed by its ions at m/e = 43 and 45 presented in Fig. 9.4a.

Table 9.2. Quantitative measurement of the product fractions formed by heating the MAn—IPAc alternating copolymer to 500°C under TVA conditions.

No	Fraction	%
1	Condensable gases and liquid fraction	34.5
2	Cold ring fraction (tar)	37
3	Residue	13
4	Non-condensable gases (by difference)	15.5



Key

——————— 0°C
— — — — — -45°C
- - - - - - - — -75°C
— - — - — - -100°C
— - - — - - - -196°C

ig. 9.3 TVA curve for MAn—IPAc copolymer sample heated in vacuum to 500°C at 10°C/min.

The curve shows that most of the acetic acid is formed in the first stage of decomposition. The evolution of carbon dioxide which is the major degradation product after acetic acid is shown in Fig. 9.4b. It is formed in a small amount in the first degradation stage and in a large amount in the second stage of decomposition. The evolution of CO_2 in the first stage could be due to the breakdown of acetate radicals.

Ketene, another product of decomposition of these radicals is also observed at this stage. Acetate radicals are known to decompose at a lower temperature than acetic acid which is a source of ketene only at higher temperatures.

The formation of 4,4-dimethyl-2- cyclopentene-1-one, is shown in Fig. 9.4c through the lines 67, 95 and 110, however the ions of masses 67 and 110 can also be formed from other isomers of dimethyl cyclopentene -one. Similarly, Fig. 9.4d shows the formation of methyl 2,5-furandione which is represented by lines 54, 98 and 112, while 2,5-furandione also accounts for ions at 54 and 98.

The aromatic compounds are formed in two stages, a small quantity in the region 200 to 300°C and the majority are formed above 350°C. Fig. 9.4e shows the formation of 1,3-dimethylbenzene (m/e = 91, 105). Again, a small quantity is formed in the region 200 to 300°C but most is formed above 350°C. The other alkyl substituted aromatic compounds, with molecular mass above 130, can not be detected clearly because signal noise obscures the low intensity of ions produced.

Non-condensable products are also formed. The main product is carbon monoxide together with small amount of methane. Carbon monoxide is formed in the region 250-400°C (Fig. 9.4f), and is due to anhydride ring

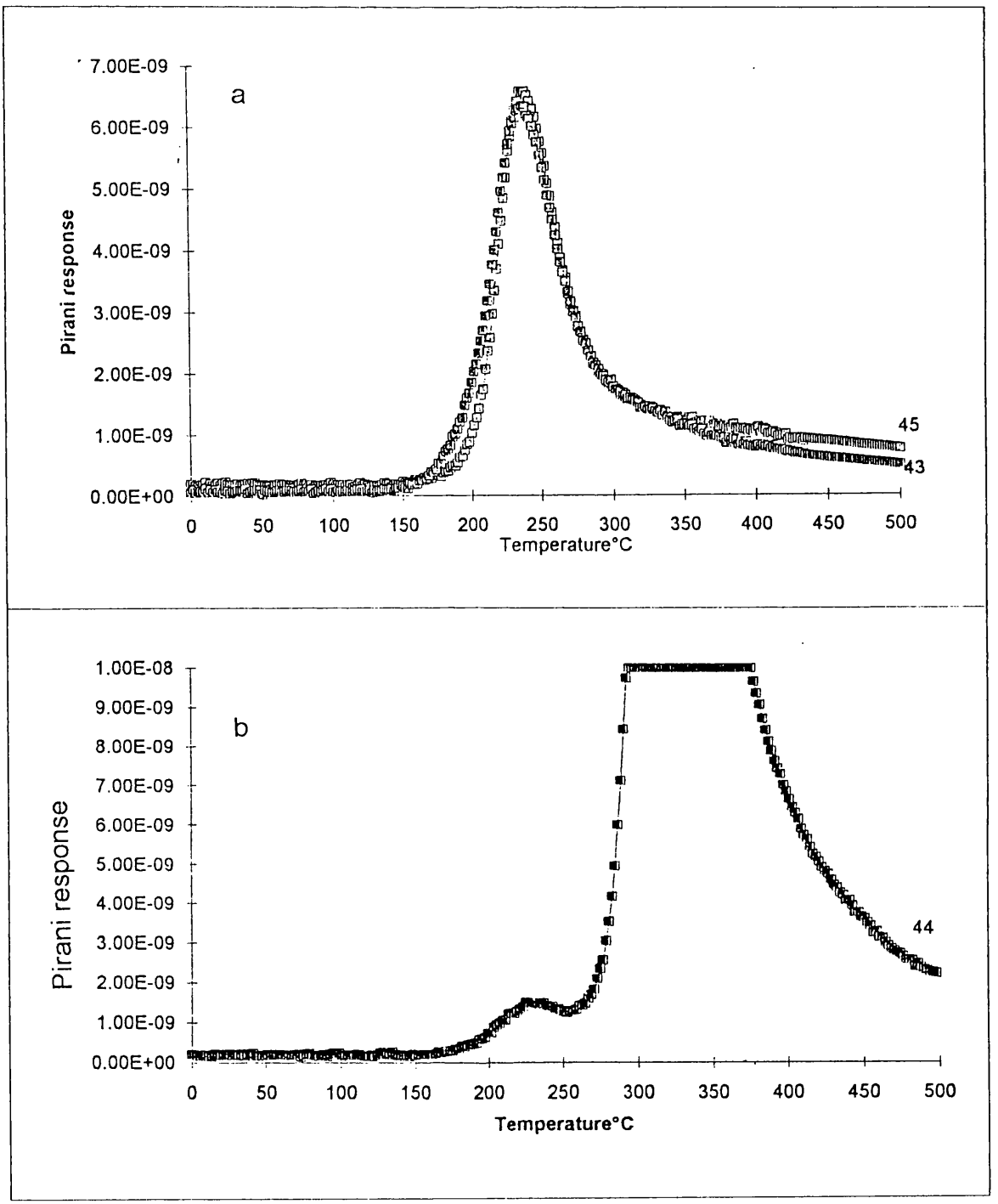


Fig. 9.4 The formation pattern of main degradation products of MAn—IPAc copolymer (Heating rate 10°C/min up to 500°C) under TVA conditions

a: Formation of acetic acid through (m/e = 43 and 45)

b: Formation of CO_2 through (m/e = 44).

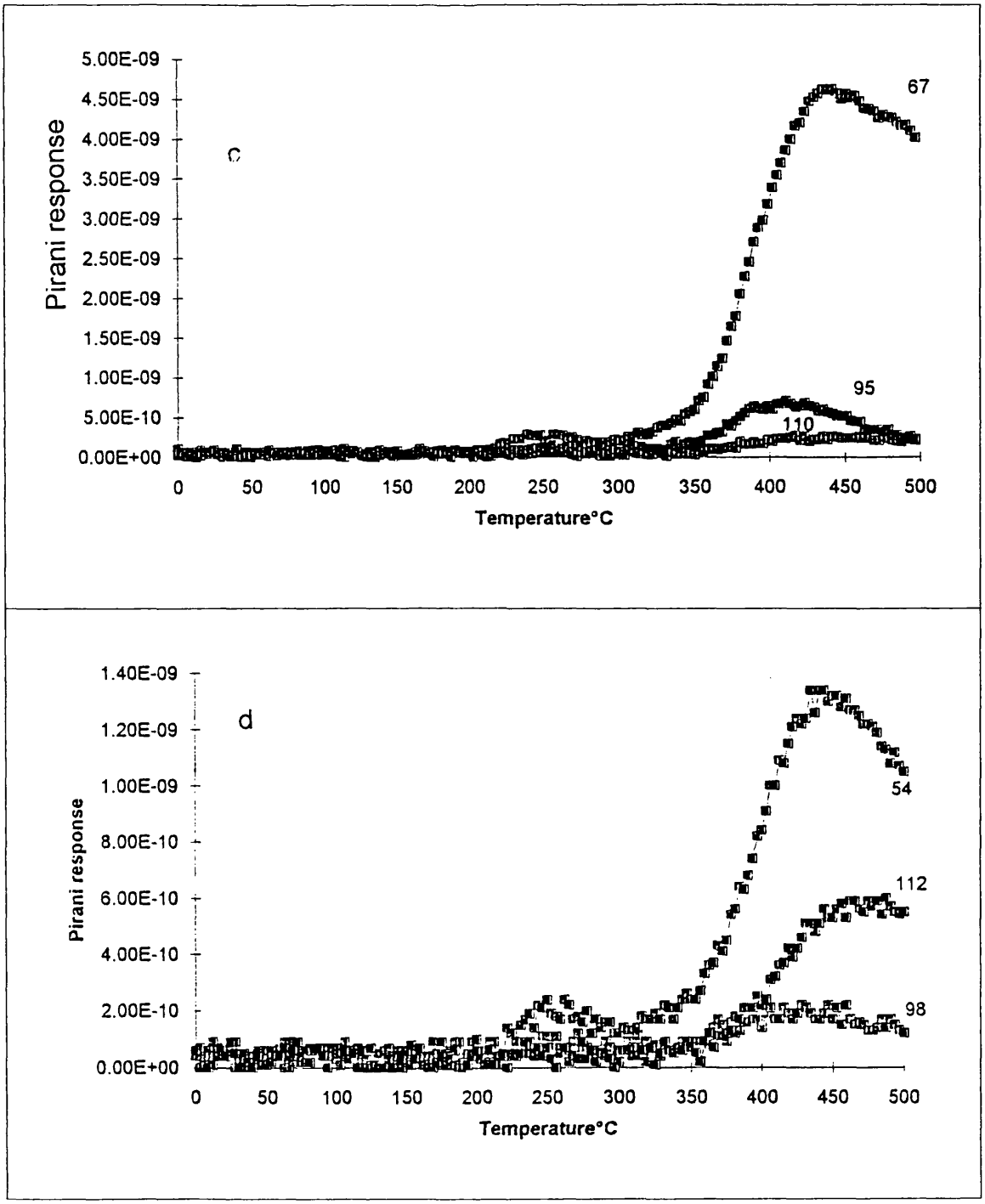


Fig. 9.4 Continued

c: Formation of 4,4-dimethyl-2-cyclopentene-1-one and other isomers through (m/e = 67, 95 and 110).

d: Formation of methyl 2,5-furandione and other isomers through (m/e = 54, 98 and 112).

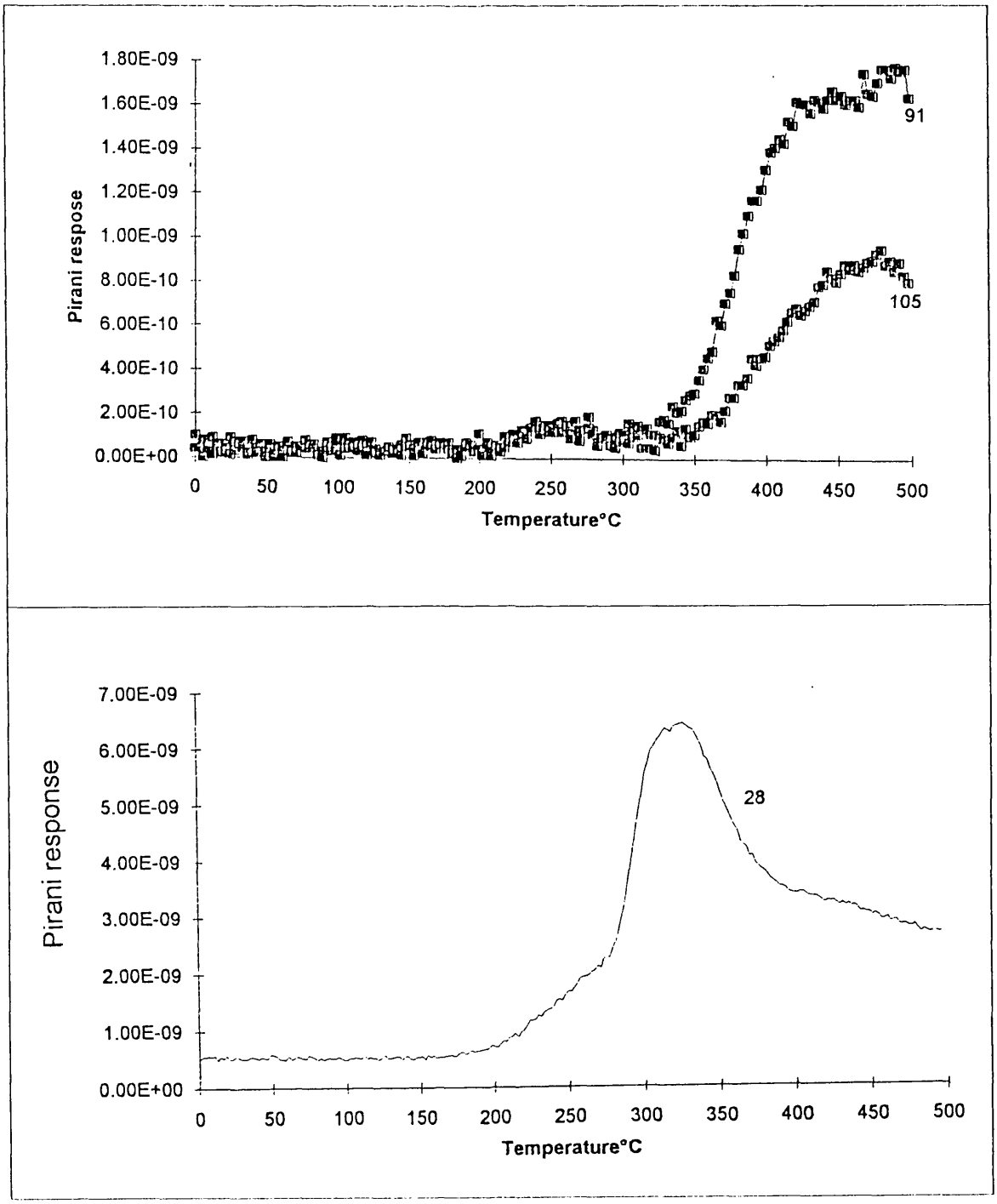


Fig. 9.4 Continued

e: Formation of 1,3-dimethylbenzene through (m/e = 91 and 105)

f: Formation of carbon monoxide through (m/e = 28).

breakdown which is an important source of CO_2 and CO at these temperatures.

SUBAMBIENT THERMAL VOLATILISATION ANALYSIS

After the TVA experiment the degradation products were collected in fractions: residue , cold ring fraction (CRF), liquid fraction and condensable gases. The condensable gases and liquid fraction collected in the liquid nitrogen trap of the vacuum system, were first separated into fractions by the SATVA method. Mass spectrometric analysis was carried out during the SATVA separation by bleeding some of the evolved products to the mass spectrometer which is coupled to the TVA system. The condensable gases were also analysed by IR spectroscopy.

The SATVA curve illustrated in Fig. 9.5, shows five peaks. The first peak is due to acetone used as a solvent, where the second peak consists of mainly of carbon dioxide.

Peak 3a which is overlapped with peak 3b and 4 is due to a mixture of various products, e.g. acetic acid, ketene, and water. Peaks 3b and 4 were collected as a liquid fraction and analysed by IR spectroscopy.

Table 9.3 summarises the products identified in various fractions separated by SATVA. In case of the liquid fraction, only highly volatile products which are identified by IR spectroscopy and on-line mass spectrometry are listed, while the less volatile products analysed by GC-MS are listed separately in Table 9.6.

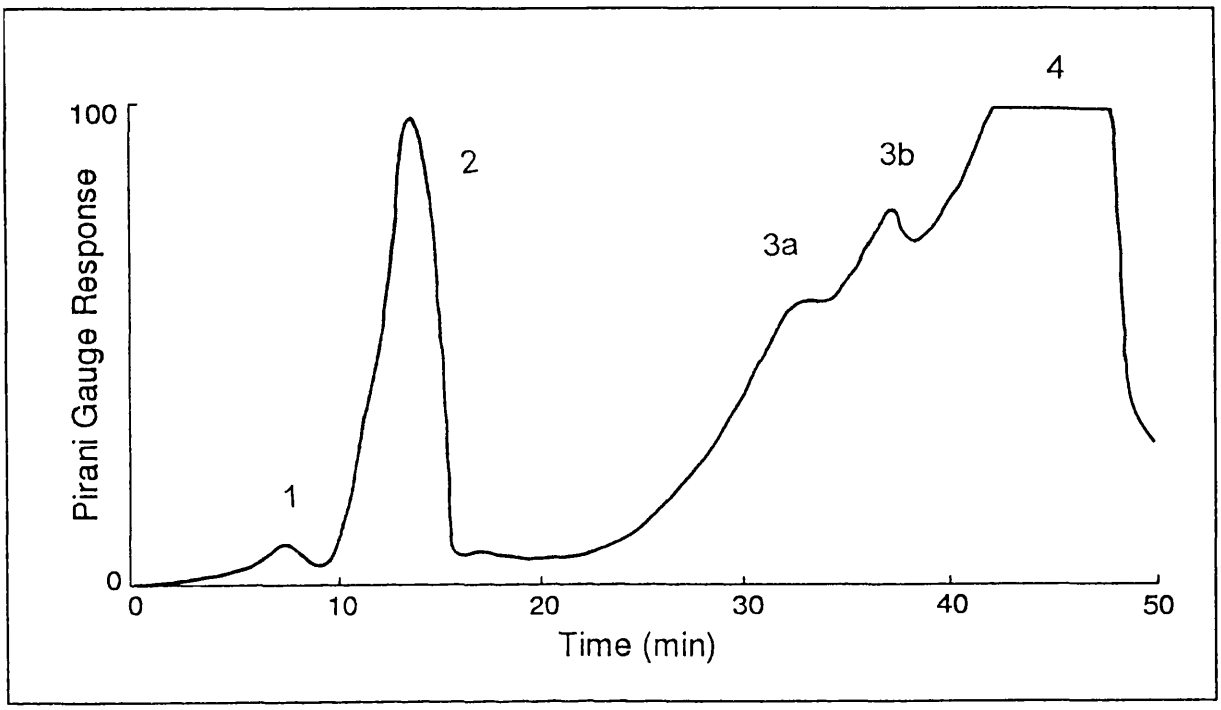


Fig. 9.5 SATVA curve for separation of the condensable volatile degradation products from degradation under TVA conditions to 500°C for MAn—IPAc copolymer.

Table 9. 3. Products of thermal degradation of MAn—IPAc copolymer heated up to 500°C at 10°C/min under vacuum suggested by the listed methods.

Noncondensable at -196°C	Condensable volatile Gases	Liquid Fraction	Cold ring fraction	Residue
MS only	IR & MS		IR MS & GC-MS	IR only
CO CH_4 hydrogen	CO_2 ethane propene ketene isobutene	acetic acid 2,5-furandione toluene, xylene trimethylbenzene	acetate groups anhydride, relatively small aromatic contents and ketone groups	black involatile char contains cross linked aromatic rings and unsaturated ketones

COLD RING FRACTION

The cold ring fraction (CRF) is composed of dark brown products condensed on the upper part of the degradation tube. The CRF was collected using a suitable solvent and transferred to a weighed bottle. After evaporation of the solvent at room temperature, the weight of cold ring fraction was determined. CRF which is a main degradation fraction (37% of the initial weight of the polymer) is mainly formed in the second stage of degradation. This fraction was examined by IR spectroscopy and by mass spectroscopy using a probe heated to different temperatures.

The IR spectrum of CRF which shows different features from that of the original copolymer (Fig. 9.6a) is shown in Fig. 9.6b. The assignments of the main absorption peaks of the copolymer are presented in Table 9.4. The CRF spectrum shows the presence of esters, anhydride and a relatively small aromatic content. The C=O stretching absorption at 1730 cm,$^{-1}$ the ν_a C-O-C band at 1248 cm^{-1} and the ν_s C—O—C band at 1170 cm^{-1} show the presence of ester groups. These ester groups are carried in the tar by the breakdown products formed towards the end of the first stage of degradation. The absorption at 1730 cm^{-1} differs from that of the original ester groups (1746 cm^{-1}) and can be due to ketone groups formed through the decomposition of some anhydride groups. Alternatively the ester groups could be bound to an unsaturated degraded polymer backbone. Anhydride groups are indicated by their absorptions at 1820 and 1768 cm^{-1}. The band at 1820 cm^{-1} is very weak and being shifted to a lower wavenumber compared to that in the original polymer (1855 cm^{-1}) suggests that the anhydride rings are unsaturated. The second anhydride band originally at 1790 cm^{-1} is also displaced towards lower wavenumbers (1767 cm^{-1}) for the same reason. Unsaturation (C=C) which is possibly conjugated, is responsible for the band at 1640 cm.$^{-1}$

Table 9.4. Assignment of the major peaks in the IR spectrum of the undegraded MAn—IPAc copolymer.

Band (cm^{-1})	**Assignment**
2960	CH_3 asymmetric stretch
2865	CH_3 symmetric stretch
1856, 1790	(C=O) stretch for anhydride rings
1740	C=O stretch of ester group
1720	C=O stretch of acid group
1460	CH_2 bending deformation
1440	CH_3 asymmetric bending
1375	CH_3 symmetric bending
1248	(C—O—C) symmetric stretching
1130	(C—O—C) symmetric stretching
1025	(CH—O) stretching
950	(C-CH_3) rocking
800, 605	(O—CO) bending and other deformations

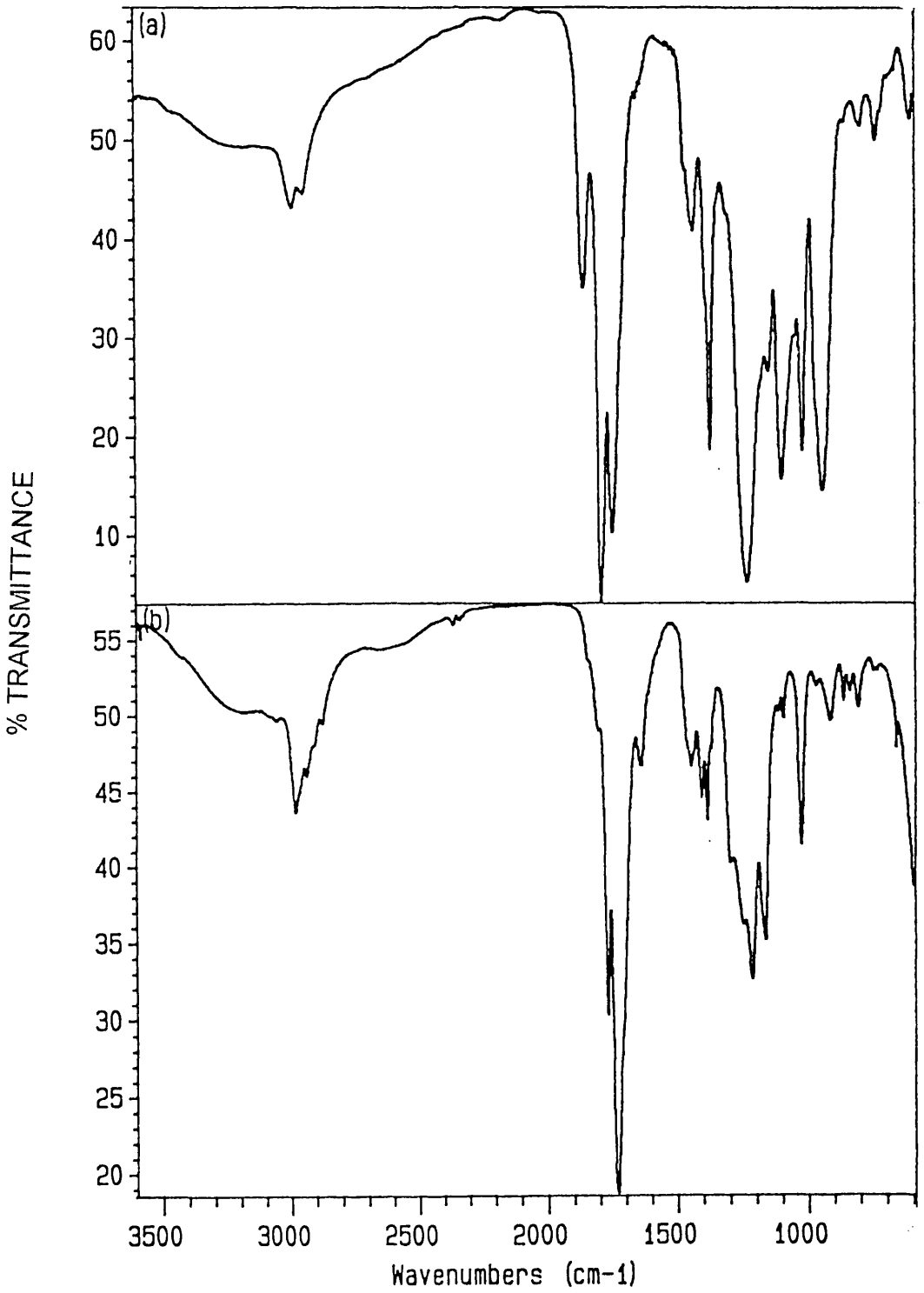


Fig. 9.6 IR spectra of (a) undegraded copolymer (b) cold ring fraction of MAn—IPAc copolymer degraded to 500°C under TVA conditions.

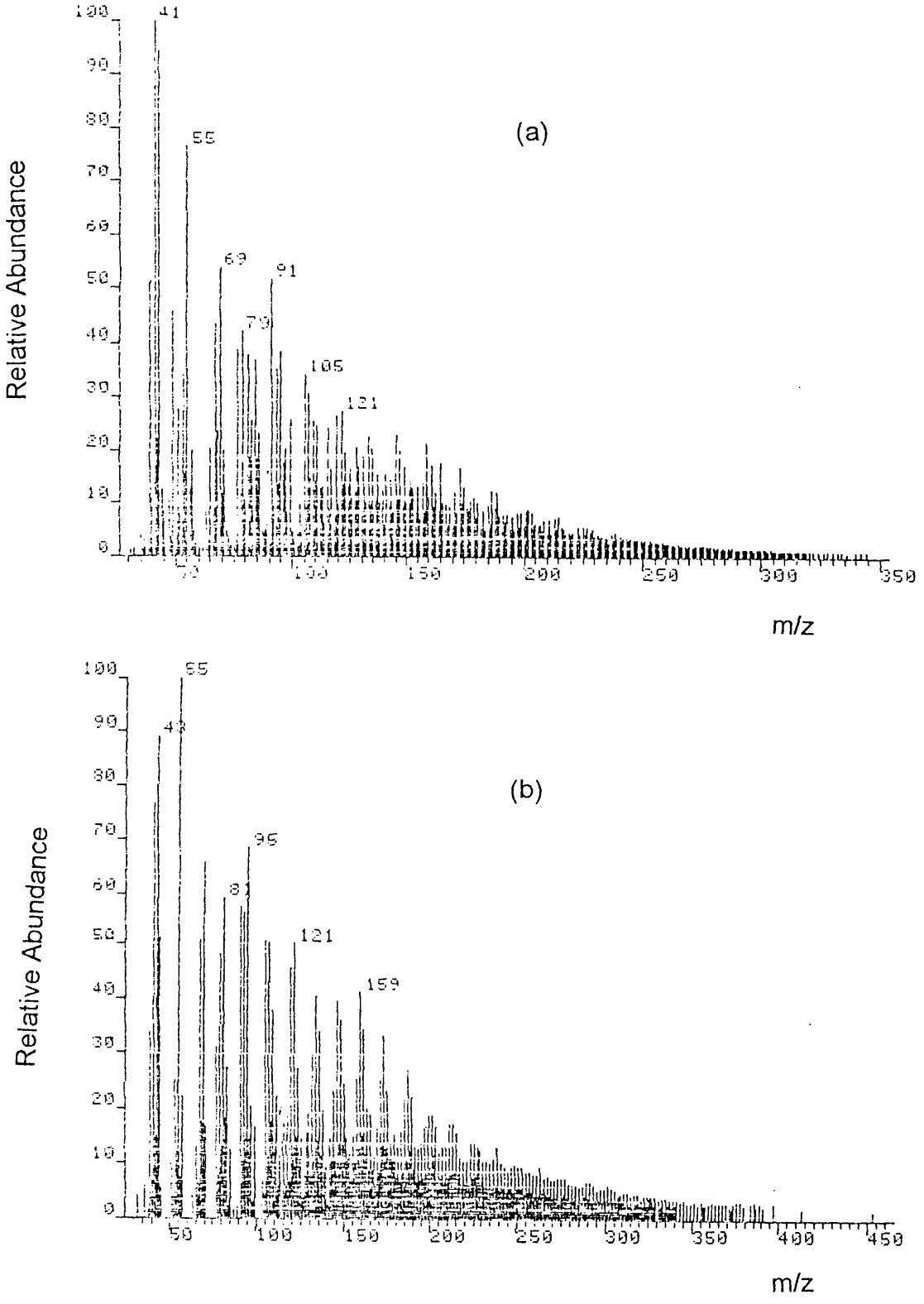
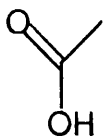
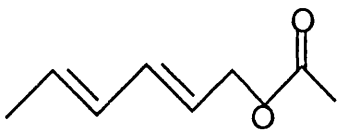
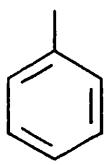
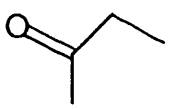
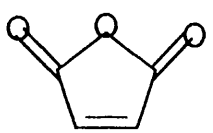
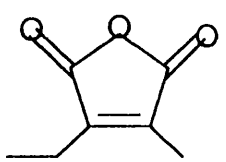
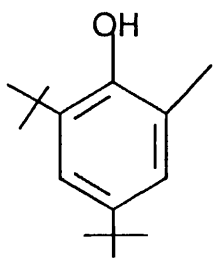


Fig. 9.7 Mass spectra of cold ring fraction (CRF) from the degradation of MAn—IPAc copolymer to 500°C under TVA conditions using probe temperatures of (a) 200°C (b) 300°C.

Tabel 9.5 The composition of the cold ring fraction (CRF) collected during the pyrolysis of MAn—IPAc copolymer (products are listed according to their relative abundance)

	Compound	MW
1		60
2		140
3		92
4		72
5		98
6		140
7		220

Aromatic rings are indicated by a shoulder at 3030 cm^{-1} and in the finger print region through the out of plane bending of four H atom (750 cm^{-1}), three H atoms (810), two H atoms at (850 cm^{-1}) and one H atom (916 cm^{-1}). The pattern of substitution here shows that the aromatic rings are quite substituted.

The cold ring fraction was also examined by mass spectrometry using a probe heated to different temperatures which gave a complex spectrum (Fig. 9.7) indicating a mixture of materials of molecular weight up to 400. The CRF was also examined by GC-MS, the identified products are being listed according to their relative abundance in Table 9.5.

POLYMERIC RESIDUE

The MAn—IPAc copolymer does not volatilise completely at 500°C, but leaves a considerable amount of black involatile residue. The amount of residue left after the TVA experiment was 13% relative to the initial weight of polymer (Table 9.2). The IR spectrum of the residue is illustrated in Fig. 9.8b.

The spectrum shows the presence of anhydrides groups through their C=O absorptions at 1830 and 1768 $cm.^{-1}$ The main bands of the anhydride groups are also displaced towards the lower wavenumbers, but the displacement is smaller than in the case of the cold ring fraction. However the reason is the same, the fact is that they are linked to the partly unsaturated polymeric backbone. The fact that anhydrides survive up to 500°C is quite unexpected given the experience with other anhydride groups such as those formed in the PMAA thermal degradation. The presence of anhydride in the residue at 500°C has already been reported, however, for the MAn—VA copolymer (33).

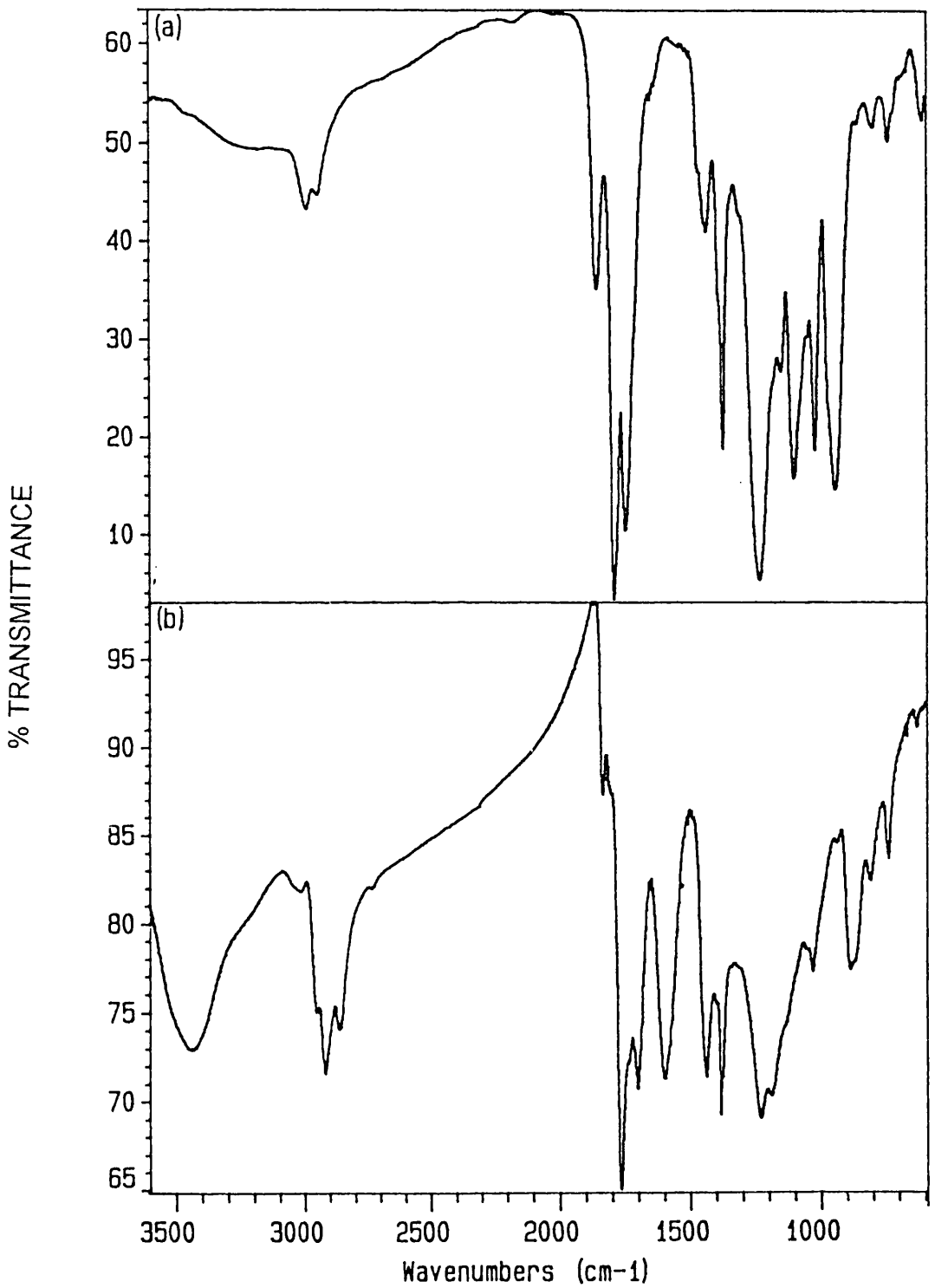


Fig. 9.8 IR spectra of (a) undegraded copolymer (b) residual fraction of MAn-IPAc copolymer degraded to 500°C under TVA conditions.

An interesting feature of the spectrum of the degraded polymer is the appearance of acid groups through the breakdown of the anhydride rings. The acid groups are evident by the broad OH stretching around 3550 cm^{-1} and by the ν C=O at 1710 $cm.^{-1}$ The ν OH band at 3550 cm^{-1} is characteristic of free (unassociated) OH groups. The ν C=O of the free unassociated COOH is expected at 1760 $cm.^{-1}$ The ν C=O absorption of a dimer associated by H bonding is expected at 1710 $cm,^{-1}$ but this assignment conflicts with the observed ν OH at 3550 cm^{-1} which shows unassociated groups. The only sound explanation is that the ν C=O at 1710 cm^{-1} is due to COOH groups attached to an unsaturated backbone (94).

Another feature of the spectrum is the high content of aromatic rings evident by their main absorptions at 3020, 1604, and at 1450 $cm.^{-1}$ The aromatic rings also show the out of plane bending of four and five C—H groups (740 cm^{-1}), three C—H groups (810 cm^{-1}), two (860, shoulder) and one C—H group (890 cm^{-1}). The substituted pattern suggests that aromatic rings are quite substituted. The bands at 1604 and 3070 cm^{-1} indicate a small contents of unsaturation (double bonds) present in the system.

In the case of poly(isopropenyl acetate) all the polymer sample degrades completely by 400°C leaving a negligible amount of residue. In the case of the MAn—IPAc copolymer, however, a significant amount of residue is observed, probably due to the development of cross linking and condensed aromatic rings which considerably enhance the stability of the copolymer.

CHARACTERISATION OF CONDENSABLE PRODUCTS

After the TVA experiment carried out under vacuum, the condensable gases and the liquid fraction were collected and weighed for the quantitative determination of the material balance (Table 9.2).

Table 9.6 The composition of the liquid fraction collected during the pyrolysis of MAn—IPAc copolymer. The products are listed according to their relative abundance

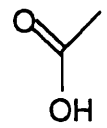
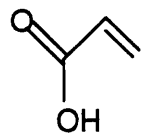
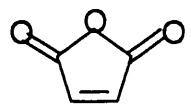
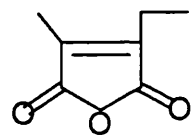
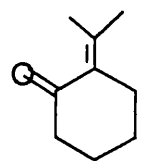
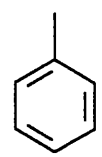
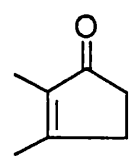
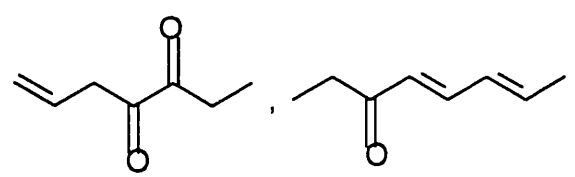
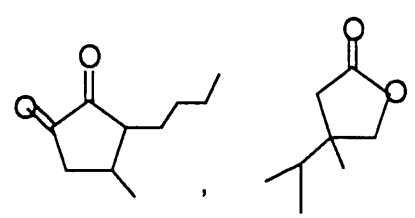
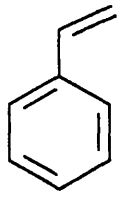
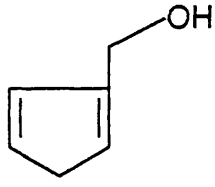
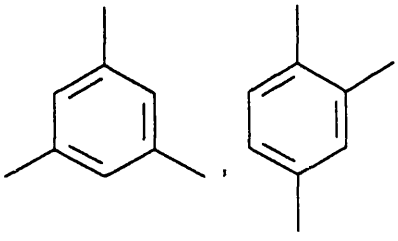
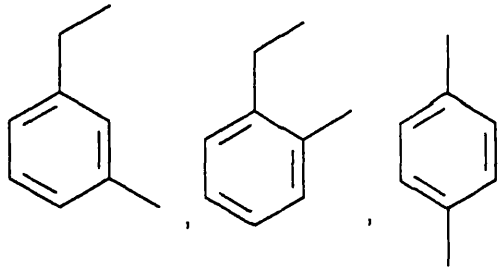
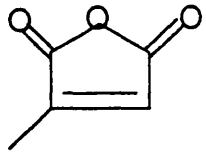
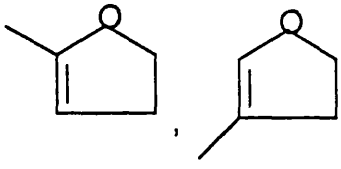
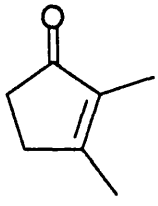
	Products	MW
1		60
2		72
3		98
4		140
5		138
6		92
7		110
8		126
9		156

Table 9.6 (continued)

Products	MW
11 	104
12 	98
13 	120
14 	120
15 	112
16 	96
17 	110

The condensable gases and the liquid fraction products were analysed by the SATVA method already described in the previous section. The less volatile products were analysed by GC-MS technique, in conditions which are described in Chapter 2.

The products of liquid fraction analysed by GC-MS are listed according to their relative abundance in Table 9.6. As can be seen the major products (after acetic acid) in the liquid fraction are furandione (3), alkyl-substituted furandione (4) and toluene (6). Important products are dimethylcyclopentenone (7), 5-membered alkyl-sustituted lactones (9) and esters of unsaturated acids.

STUDY OF STRUCTURAL CHANGES IN COPOLYMER DURING DEGRADATION

The structural changes in the MAn—IPAc copolymer occurring during degradation were followed by heating a portion of film in dynamic or isothermal conditions which was then studied by spectroscopy using the FTIR diffusion reflection technique. The polymer sample was cast as a film by pouring a concentrated solution in acetone uniformly on to a stainless steel plate. The acetone was allowed to evaporate at room temperature. The apparently dried film was then evacuated in a vacuum oven at 40°C for 24 hours to constant weight. The film was then heated up to 80°C to evaporate any trace of solvent.

In a dynamic experiment the changes in polymer structure were followed by heating the polymer film at a rate of 10°C/min to a chosen ceiling temperature in vacuum. The film was then cooled quickly to room temperature and the spectrum was recorded. In some cases the spectra were subjected to automatic deconvolution, a processing mode in the

existing software.

The structural changes upon heating at temperatures from 200 to 440°C are illustrated in Fig. 9.9(b-f). The spectrum of undegraded copolymer (Fig. 9.9a) shows main absorption bands which have already been summarised in Table 9.4.

Upon heating the polymer to 200°C (Fig. 9.9b), the only change in the spectrum is the appearance of unsaturation (1653 cm^{-1}). The polymer heated up to 240°C shows significant changes in the ester bands (Fig. 9.9c). The ν C=O of the ester has disappeared almost completely or it is left as a shoulder barely noticeable in the width of the anhydride band. The bands at 1440 and 1371 cm^{-1} due to the CH_3 groups are also extensively reduced suggesting the loss of acetate methyl groups. The band at 1653 cm^{-1} due to conjugated double bonds has increased greatly through the loss of ester groups from the polymer chain. The formation of the 1653 cm^{-1} band coincides with the appearance of the band at 990 cm^{-1} which can be regarded as due to the trans double bond encountered in conjugated systems. The carbonyl absorptions ν C=O of maleic anhydride, initially present at 1856 and 1790 $cm,^{-1}$ are shifted to lower wavenumbers, now at 1830 and 1770 cm^{-1} suggesting that the anhydride groups are bound to an unsaturated backbone.

This lowering of carbonyl absorption is also indicative for conjugation of double bonds without any backbone scission (100), which will be further discussed in relation to the isothermal studies carried out at lower temperature. The complete loss of ester groups at this temperature confirms the TVA results that the first stage of degradation (160-250°C) indicated in TVA curve corresponds only to the loss of ester groups. Above 250°C the material containing double bonds "conjugated with anhydride rings" is an entirely different material than the starting one.

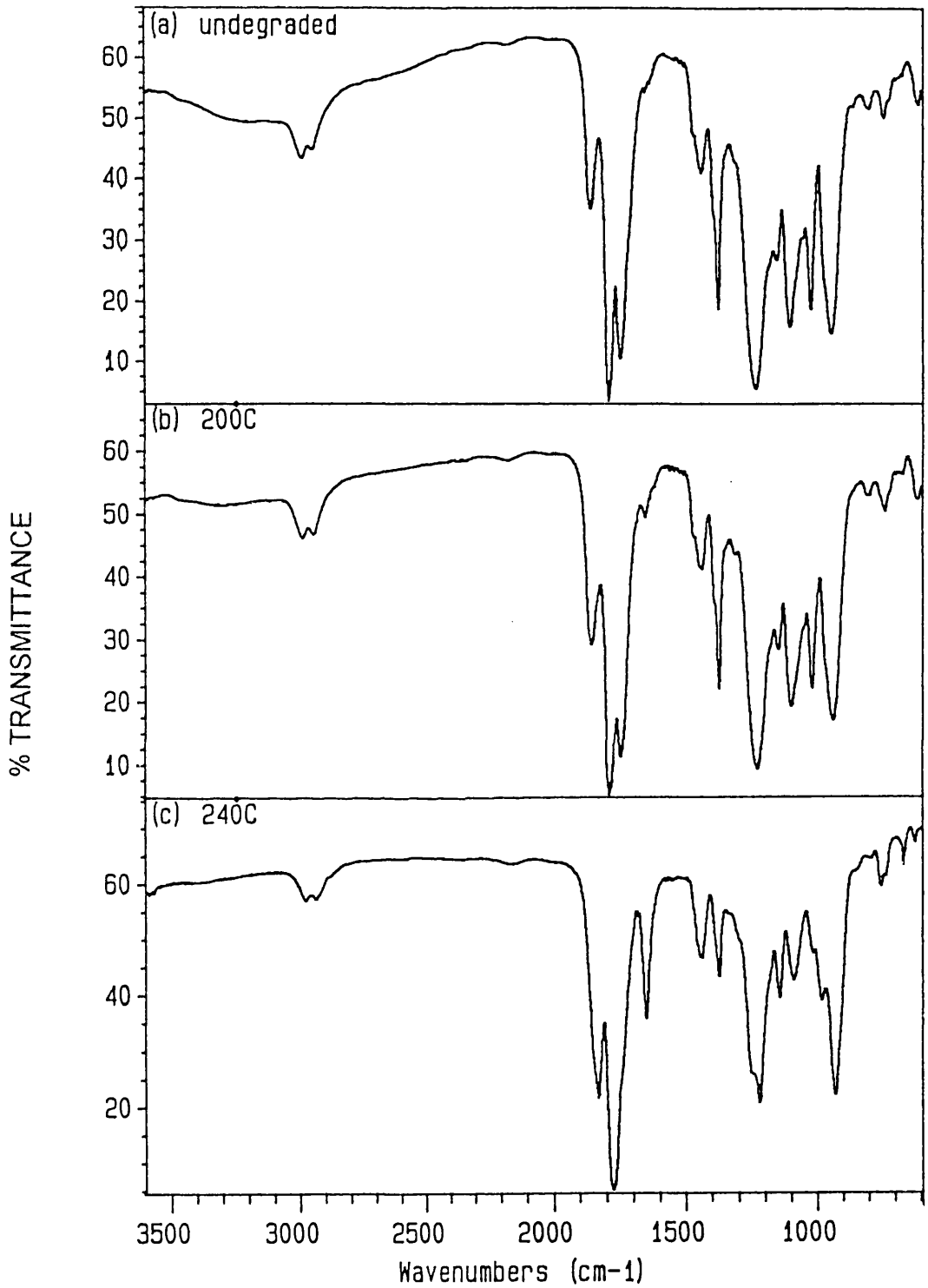


Fig. 9.9 Infrared spectra of the MAn—IPAc copolymer: (a) before and after heating in vacuum to: (b) 200°C (c) 240°C.

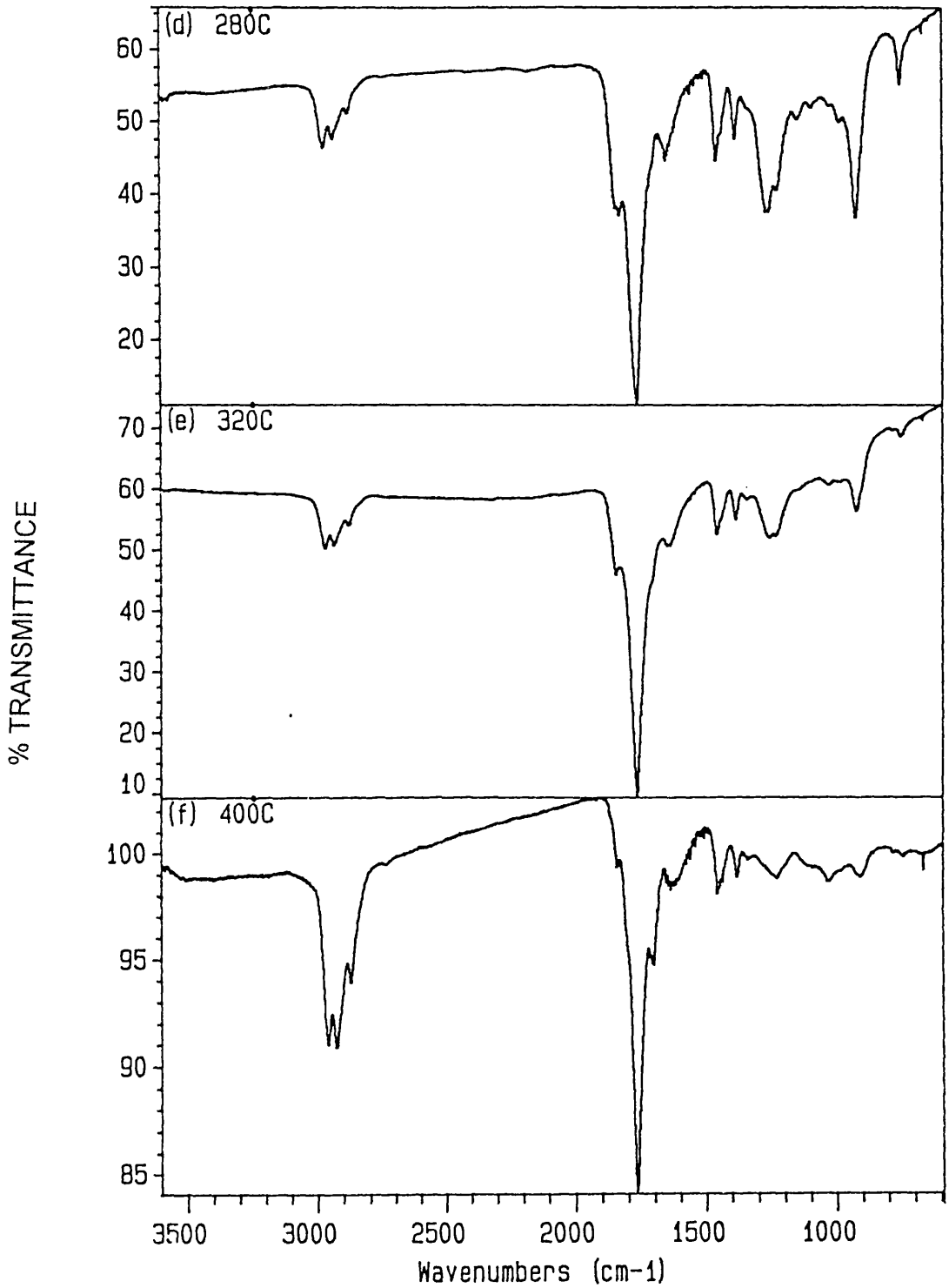


Fig. 9.9 Continued (d) 280°C (e) 320°C (f) 400°C.

At 280°C the anhydride carbonyl absorption has further decreased especially the band at 1830 cm,$^{-1}$ which indicates the breakdown of anhydride rings (Fig. 9.9d). The decrease in absorption at 1653 cm^{-1} and the appearance of a shoulder on this band at 1604 cm^{-1} shows the beginning of aromatisation in the system at the expense of unsaturation. A new band at 1264 cm^{-1} is attributable to ν_a (=C—O—C) in aromatic and vinyl system. The transformations upon heating the polymer to 320 and 360°C show little changes. It can be seen that the residual polymer is fairly stable in this temperature region, Fig 9.9e. However, there is an indication that anhydride groups continue to decompose. The evidence is the increasing ratio of the aliphatic C—H bonds to the anhydride C=O bonds.

At 400°C the spectrum (Fig. 9.9f) shows further loss of anhydride groups and some features of aromatisation (1600, 1560, 1450 cm^{-1}). The new absorption 1706 cm^{-1} which could be detected as a shoulder at 360°C but is now significant, is attributable to α,β-unsaturated ketone.

THERMAL DEGRADATION OF MAn—IPAc COPOLYMER UNDER ISOTHERMAL CONDITIONS

The thermal stability of the MAn—IPAc copolymer has also been investigated isothermally at a lower temperature, 170°C, for the confirmation of the above FTIR results and to focus attention on the effect of the less thermally stable monomer unit on the thermal behaviour of the alternating copolymer.

The alternating copolymers of maleic anhydride with vinyl acetate has been investigated previously by McNeill and Polishchuk (33) by heating at 205°C for various lengths of time in vacuum conditions. They reported that the first step elimination of acetic acid can bring structural changes in the polymer

chain, namely the formation of double bonds. Matsui and Aida (101) studied the isothermal degradation on MAn—VA copolymer at 180°C in the absence of air and concluded that complete loss of acetic acid occurred at this temperature over the period of six hours.

Experimental

The MAn—IPAc copolymer in measured quantity was dissolved in Analar acetone. A film was cast on a stainless steel plate, then dried using the same method as described previously. The plate supporting the sample was heated in the degradation tube at 170°C under vacuum for various length of time, cooled down to room temperature and the loss of weight was measured carefully. The spectroscopic changes at different times of heating were recorded by the FTIR diffusion reflection technique. The quantitative weight loss was determined as a function of the time by weighing the polymer film before and after every heating. The elemental analysis of residue was carried out with the Carlo Elba elemental analyser for the determination of the weight percentage of carbon and hydrogen.

Results

The average weight loss from several sets of experiments is shown in Table 9.7.

The whole curve for the average weight loss in the course of the six hours heating is shown in Fig. (9.10).

Table 9.8 presents the elemental composition (C, H) of the copolymer samples heated for six hours at 170°C together with expected theoretical composition if the only eliminated product was acetic acid. The experimental and the calculated results are in very good agreement.

The spectroscopic changes with the time of heating from ten minutes to six hours are compared in Fig. 9.11 (b-f), with the spectrum of undegraded copolymer in Fig. 9.11a. Fig. 9.11 (b & c) show changes upon heating the polymer for as little as 10 or 15 minutes at 170°C, respectively. The decrease in the intensity of the band at 1740 cm^{-1} C=O of an ester along with the decrease in intensities at 1370 cm^{-1} (ν_s CH_3) and 1440 cm^{-1} (ν_a CH_3) indicate the loss of ester groups. The new absorption bands at 3100 and at 1640 cm^{-1} suggest the formation of unsaturation (C=C) in the polymer chain.

Table 9.7. Average weight loss of (two samples) of MAn—IPAc copolymer on heating at 170°C under vacuum for various length of time.

Time	Average weight loss
15 minutes	13.09 %
30 minutes	16.88 %
60 minutes	22.70 %
180 minutes	27.33 %
360 minutes	30.18 %

Table 9.8. Microanalysis of residue of MAn—IPAc copolymer after 6 hours of heating at 170°C under vacuum (average values from two set of experiments)

Batch. 1.	Calculated	Experimental
% Carbon	60.86	59.12
% Hydrogen	4.34	4.51
Batch.2.	Calculated	Experimental
% Carbon	60.86	58.8
% Hydrogen	4.34	4.34

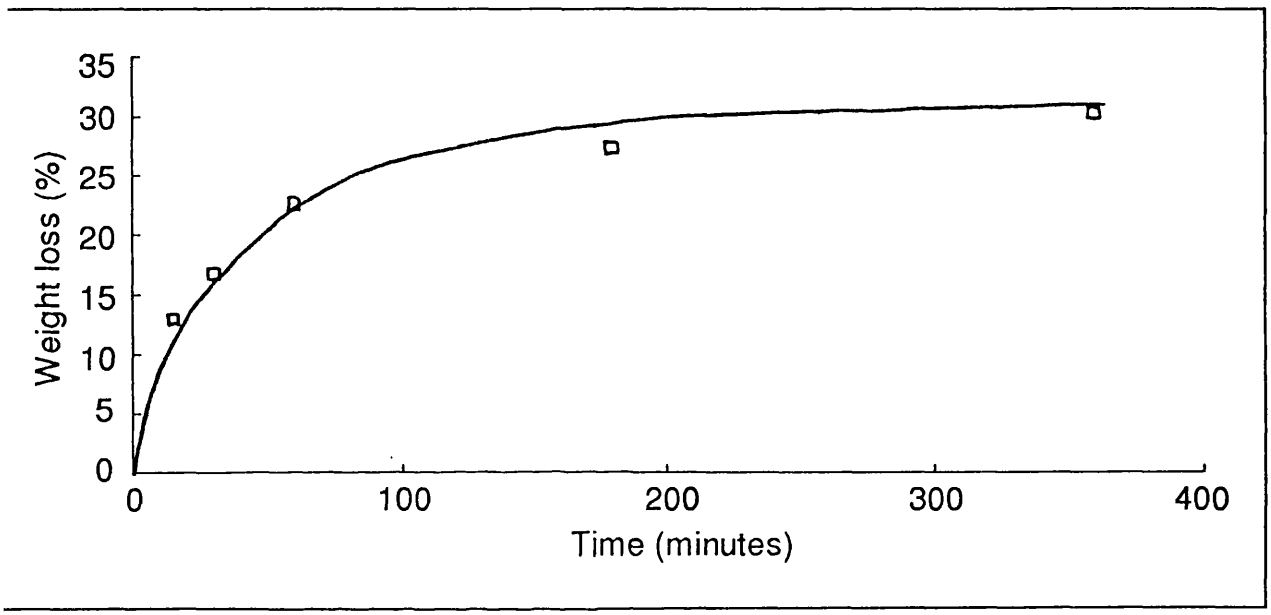


Fig. 9.10 Weight loss for MAn—IPAc copolymer on heating for up to 360 minutes at 170°C.

The identification of acetic acid by MS during the heating at 170°C suggests that the unsaturation is formed through the loss of ester groups. Upon heating the polymer for thirty minutes the carbonyl absorptions which were initially present at 1856 cm^{-1} and 1790 cm^{-1} shifted to lower wavenumbers 1840 and 1778 cm^{-1} as can also be seen in Fig. 9.11(d). Further loss of esters groups and subsequent increase in the intensity at 1652 cm^{-1} also be seen. This trend of decreasing of carbonyl absorption and loss of ester groups can be followed up on heating polymer for times up to sixty minutes Fig. 9.11e. There is also a continuous decrease of the intensity ratio of the anhydride bands originally at 1856 and 1790 cm^{-1} with the time of heating.

After heating the polymer for six hours at 170°C, the significant changes in polymer structure can be followed (Fig. 9.11f). The carbonyl absorption at 1740 cm^{-1} has disappeared completely and the unsaturation around at 1652 cm^{-1} is fully developed. The two carbonyl absorptions of anhydride are further shifted to lower wavenumbers, now at 1830 and 1770 cm^{-1} indicating conjugation with double bonds. Caze and Loucheux (102) in their investigations on MAn—VA alternating copolymer at lower temperature examined the possibility with the object of confirming their proposal of the influence of charge transfer complex on lowering of two carbonyl absorptions bands followed by the formation of conjugation with double bonds. Later this possibility was also confirmed by McNeill and Polishchuk in their isothermal studies on MAn—VA alternating copolymer. This lowering of anhydride carbonyl absorptions are not observed in case of an unconjugated double bond (102).

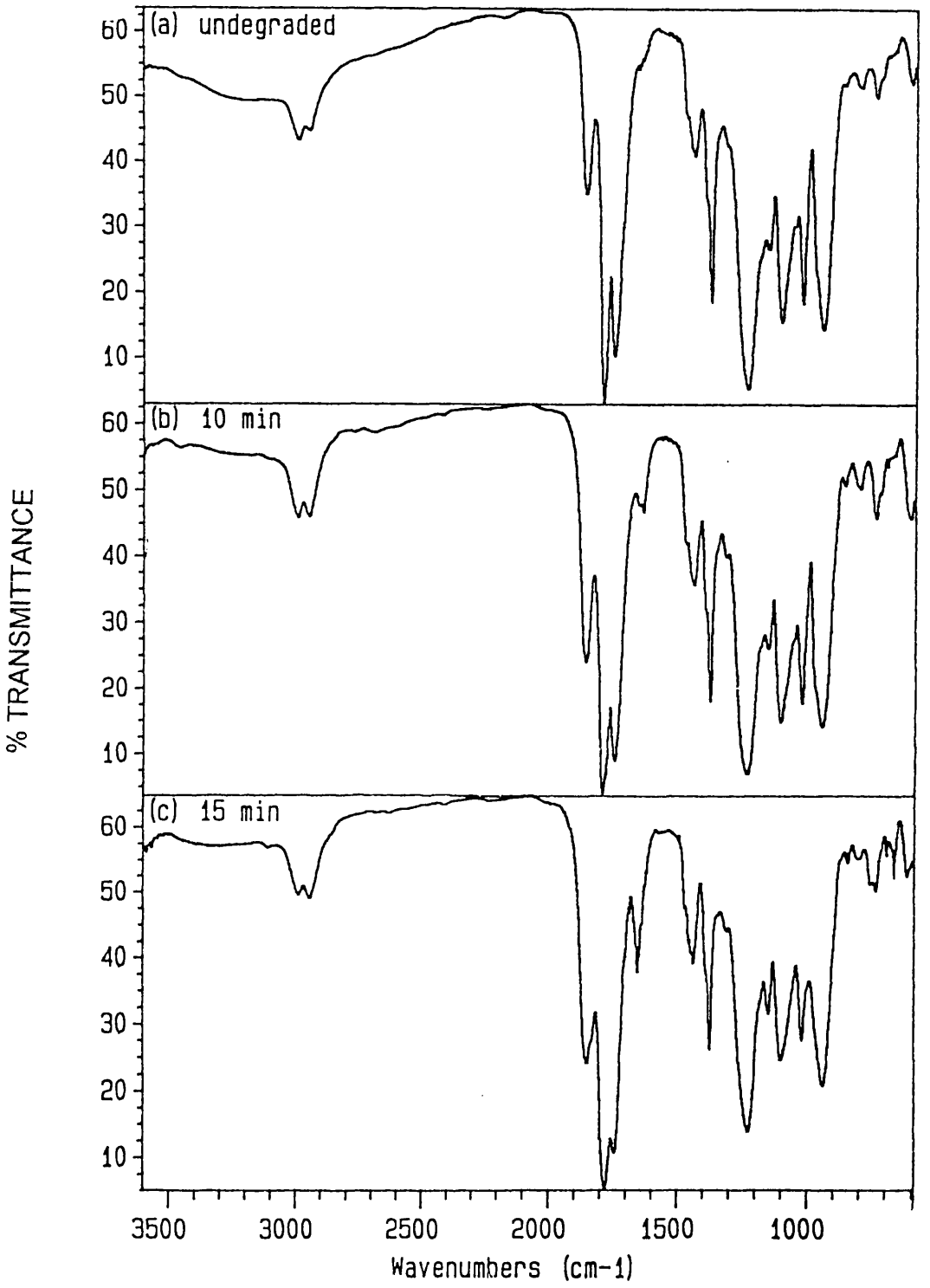


Fig. 9.11 Infrared spectra of the MAn—IPAc copolymer: (a) before and after heating in vacuum at 170°C (b) 10 min (c) 15 min.

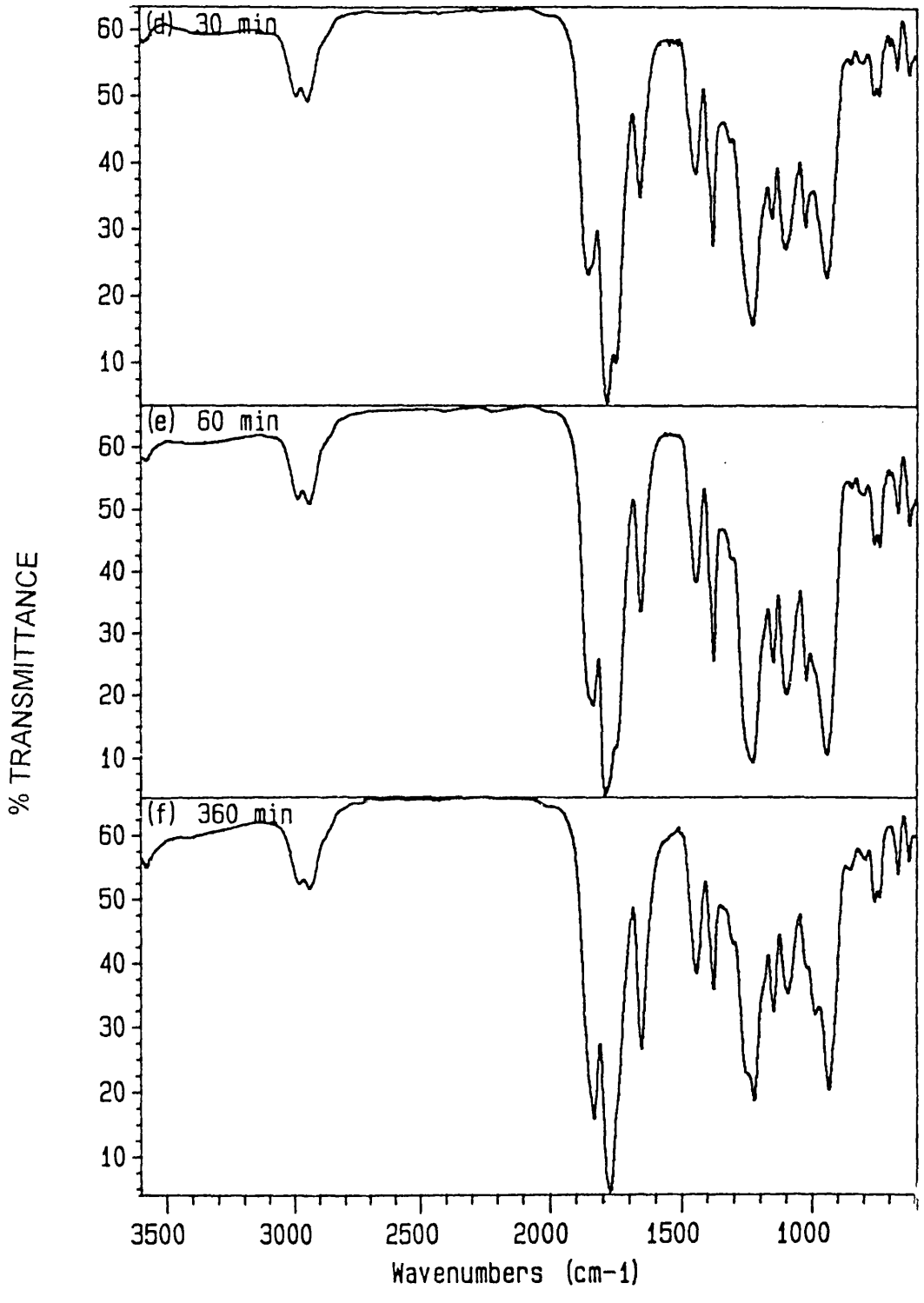


Fig. 9.11 Continued (d) 30 min (e) 60 min (f) 360 min.

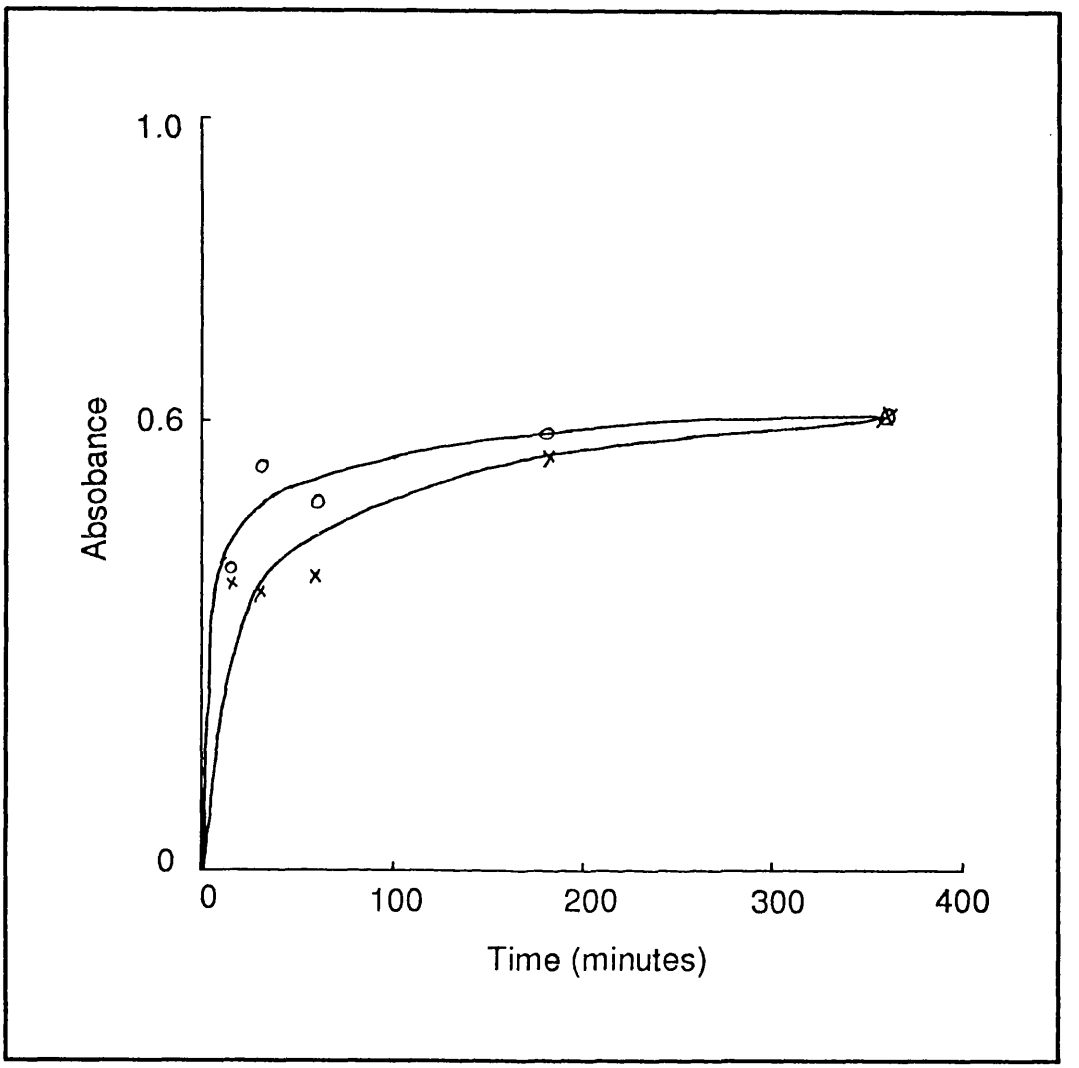


Fig. 9.12 Accumulation of double bond absorption at 1625 cm^{-1} (two samples) for MAn—IPAc copolymer on heating at 170°C for up to 360 minutes.

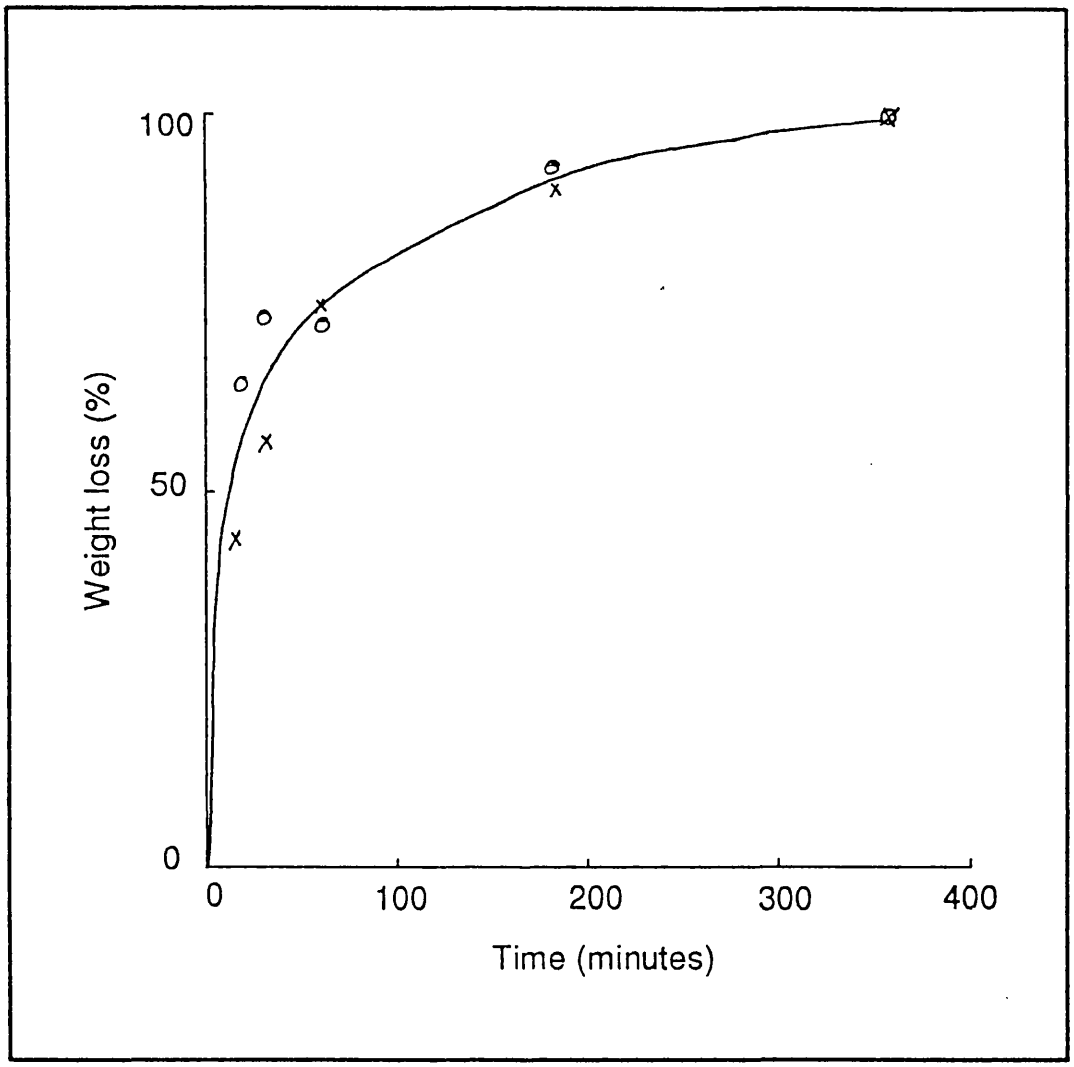


Fig. 9.13 The curve for accumulation of acetic acid with time (o) and increase of absorption intensity of double bond (C=C) at 1652 cm^{-1} (x) for MAn—IPAc copolymer on heating at 170°C for up to 360 minutes.

In the case of the present investigations on MAn—IPAc copolymer the disappearance of carbonyl absorption at 1740 cm^{-1} shows the complete loss of ester groups and the lowering of the two carbonyl absorption bands (1854 and 1790 cm^{-1}) is attributable to the conjugation to the carbonyl group of the anhydride function.

The average increase in the absorption intensity of the band at 1652 cm^{-1} from the two sets of experiments is presented in Fig. 9.12. The elimination of acetic acid from each isopropenyl unit to give a novel polymeric structure is shown in Scheme 1, reaction 1. On the basis of lowering of carbonyl absorptions, the proposed conjugation is favoured by structures II and III. Fig. 9.13 shows accumulation of acetic acid with time and increase in absorption intensity at 1652 $cm,^{-1}$ both curves gives good correlation for complete loss of acetic acid from the polymeric chain and favour the above mentioned structures.

DISCUSSION

The structure of the MAn—IPAc copolymer is polarised by the electron withdrawing effect of the anhydride C=O as in Scheme 1, I. This reduces the methine H electron density so that they can be lost more easily either in elimination reactions or through free radical attack. Meanwhile the methylene hydrogens are quite neutral as this position is not directly linked to electron withdrawing groups. Accordingly, the loss of acetic acid is expected to occur as in reaction 1 i.e. between the acetate groups and the H belonging to the maleic anhydride unit and not within the isopropenyl acetate unit. Isolated double bonds are formed at the beginning as in structure II.

Structure II could give the isomeric structure III through double bond and H migration at the expense of energy gain through the conjugated double bond system formed with the anhydride (reaction 2). Further loss of H from

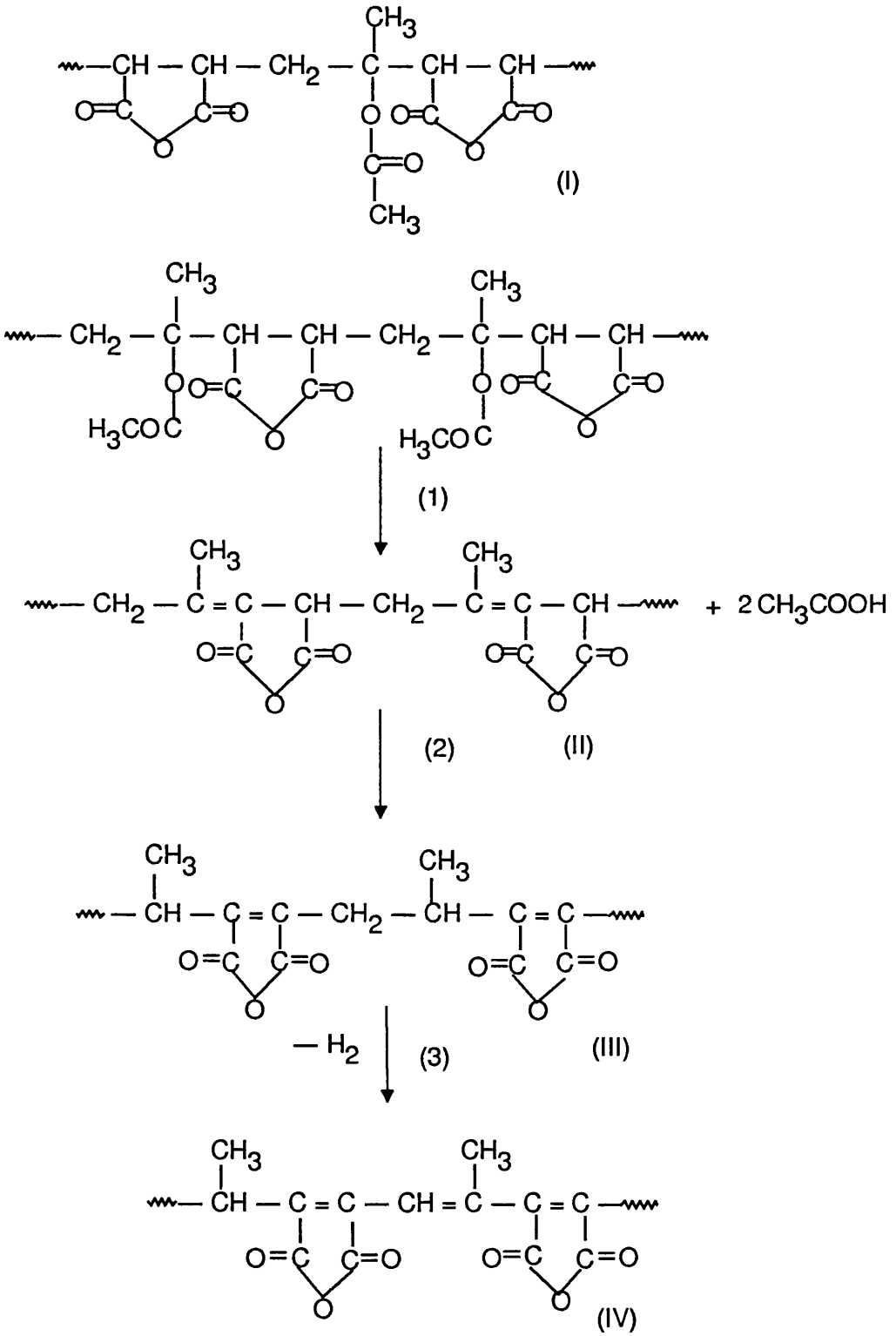
the methylene position and the tertiary C atom position (reaction 3) could lead to the structure IV which has the conjugated double bond system suggested by the spectra (1652 cm^{-1}). However, structure III is not supported by the FTIR spectra. If such a structure existed, the difference between the wavenumbers of the two C=O bands should be 45 cm^{-1} which has not been observed. This difference throughout the thermal degradation 60-70 cm^{-1} suggests that the double bond conjugated with the anhydride group is outside the anhydride ring. Hence, the elimination of H_2 leading to the conjugated system of double bonds takes place as in reaction (4) and the driving force is the conjugated energy in the copolymer backbone.

The experimental data have shown that the ratio of intensity of the first to the second anhydride C=O band increases continuously with the time of isothermal heating. It is known (100) that the first peak is stronger for cyclic anhydride groups while the second peak is stronger for acyclic anhydride groups. One possible explanation of the increased ratio of the two bands would be some rearrangements of anhydride groups as in reaction 5. Of course, during in such thermal rearrangements some anhydride groups are lost through decomposition eliminating CO and CO_2 and forming free radicals (structure VI) which can promote crosslinking.

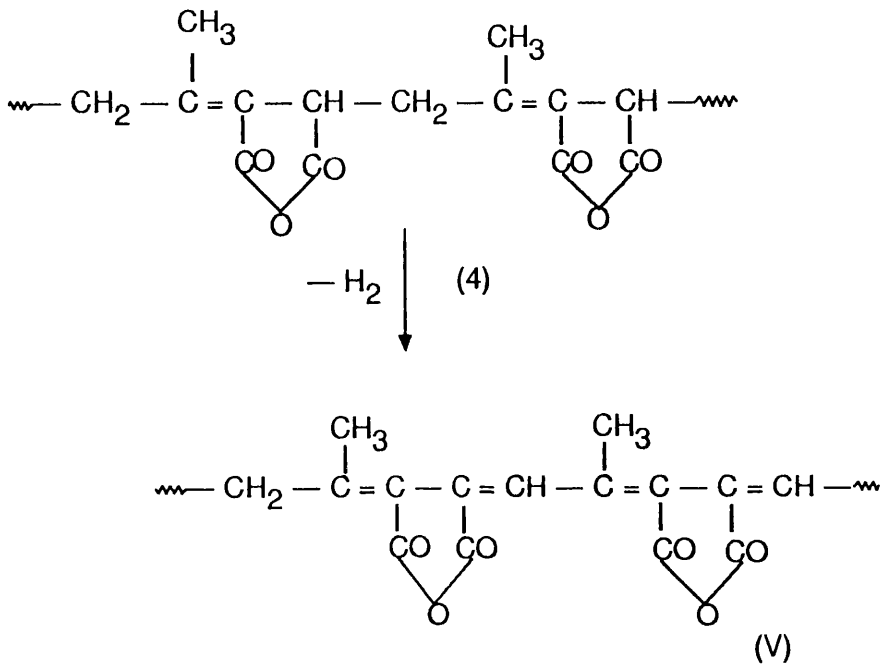
The FTIR spectra also show that the intensity of the 1652 cm^{-1} band due to the conjugated system of double bonds increases continuously up to 240°C but diminishes suddenly at 280°C as does its associated band at 980 cm^{-1} due to the ∂ CH out of plane bending of trans conjugated double bonds. Since not much aromatisation is observed at this stage, the probable explanation is the distortion of the conjugated double bond system by scission and crosslinking, both phenomena being brought about by the decomposition of the anhydride groups. Indeed weight loss at this stage is 45% as indicated by the TG curve.

Mechanism of Degradation for Maleic anhydride—Isopropenyl acetate Copolymer

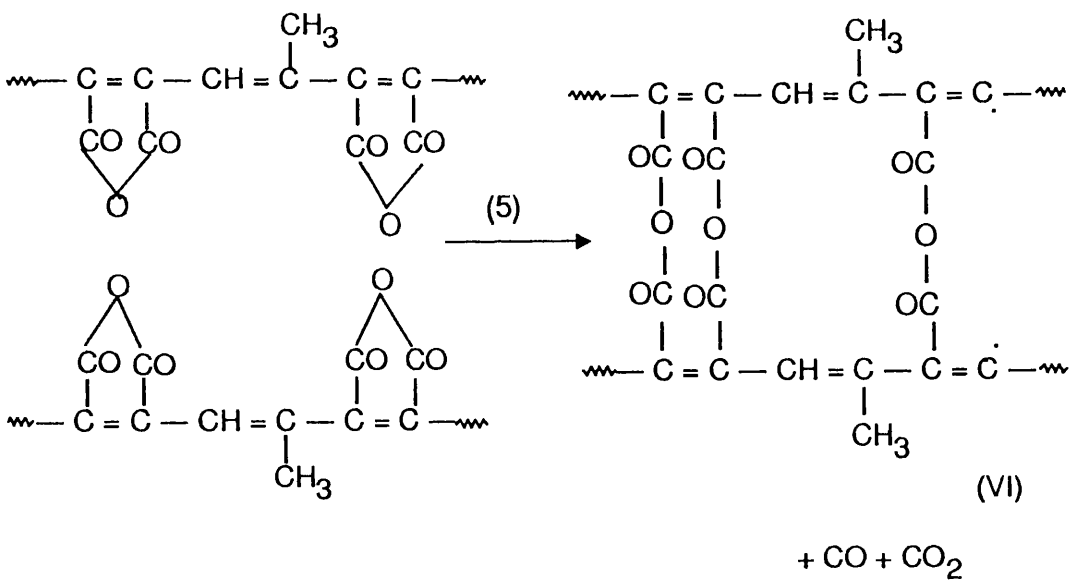
Scheme 1



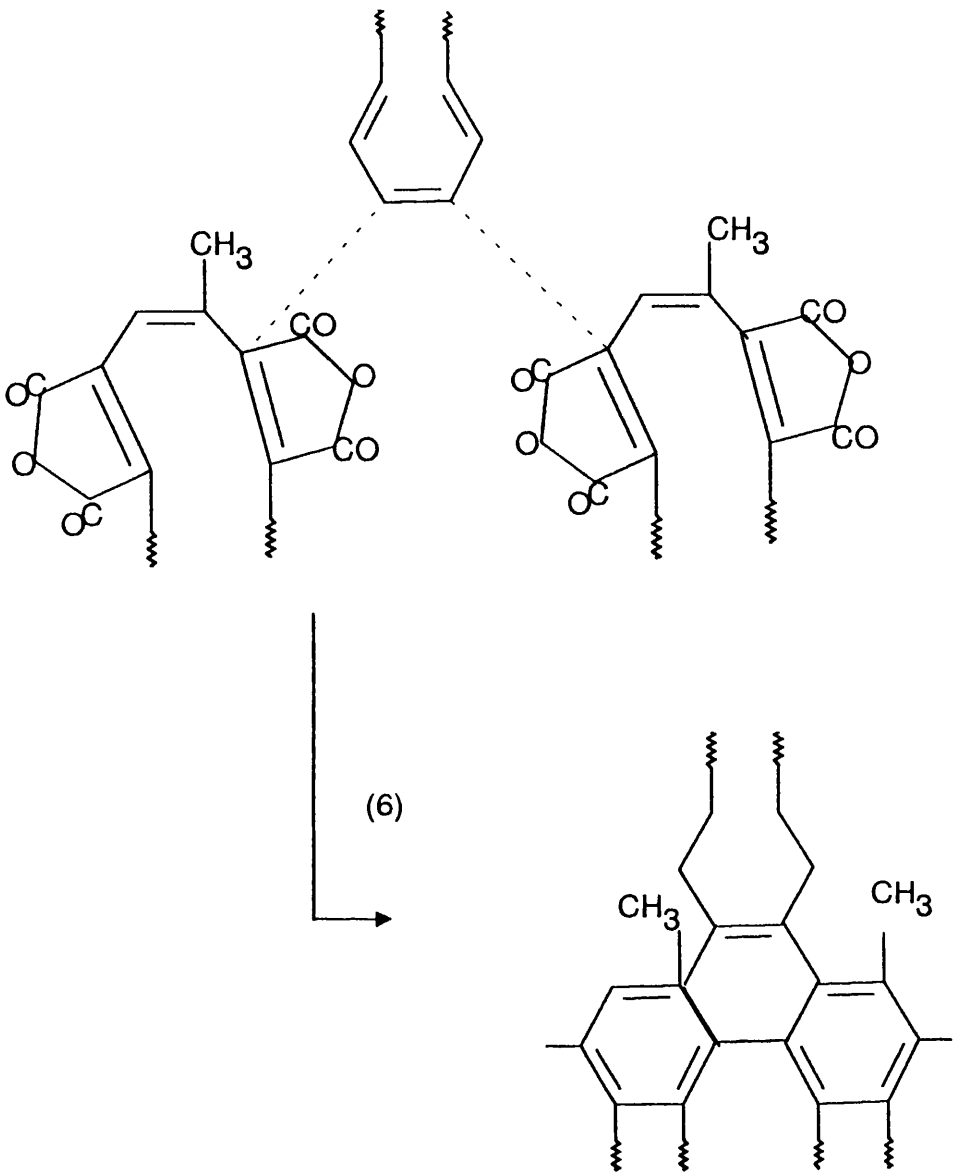
Scheme 1 (continued)



Scheme 2



Scheme 2 (continued)



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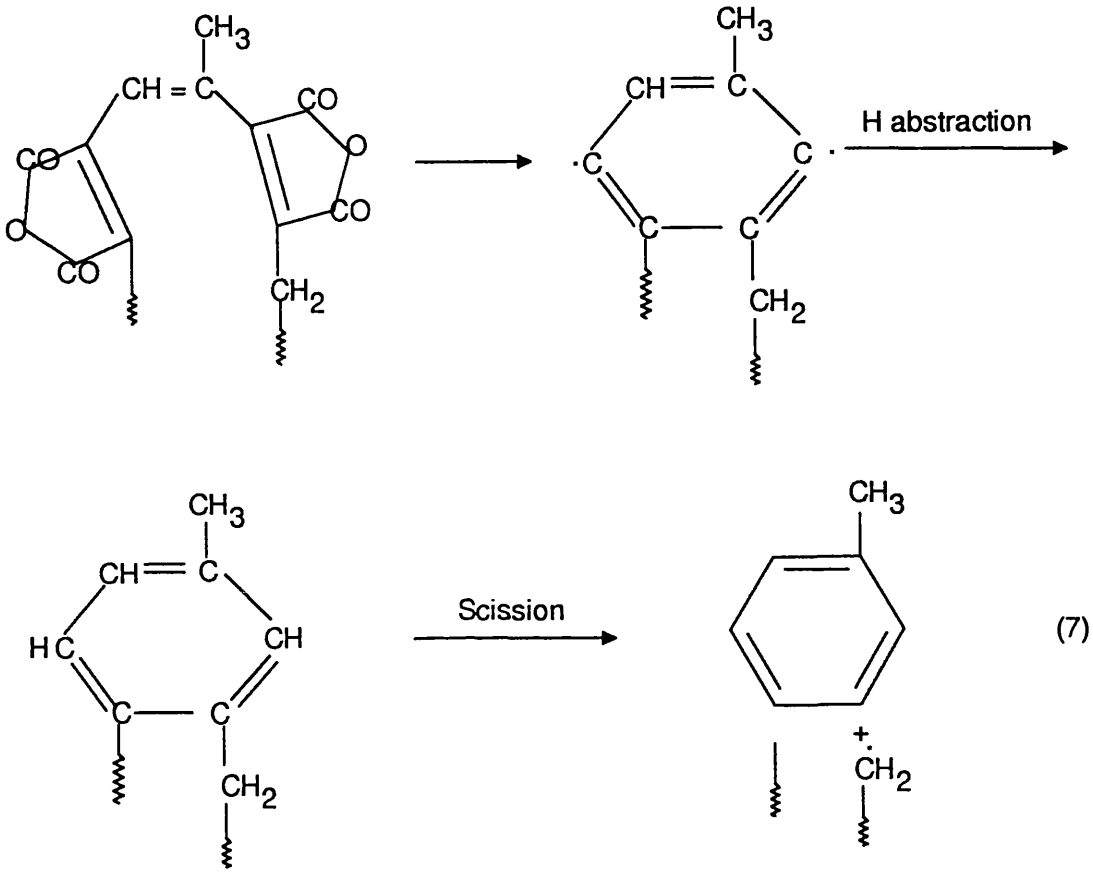


(7)

Reaction 6 tries to explain through the decomposition of anhydride rings the intermolecular formation of condensed aromatic rings which are retained in the char. Reaction 7 tries to explain the formation of toluene through intramolecular condensation following the decomposition of anhydride rings. The reaction mechanism for minor degradation products is already given in Chapter 8.

CONCLUSION

The thermal degradation of the alternating MAn—IPAc copolymer in vacuum up to 500°C has been studied with the aim of elucidating the newly-formed polymer structure since it is known that both comonomers have the tendency of losing the functional groups producing thereby long sequences of conjugated double bonds.

The use of thermal methods has shown that the MAn—IPAc copolymer degrades in two stages. The first , between 150 and 250°C, is due to the complete loss of acetate groups from the IPAc units, which brings about the formation of isolated double bonds in the polymer backbone. The FTIR studies confirm the presence of anhydride groups with α,β-unsaturation external to the ring.

In the second degradation stage, between 250 and 500°C, a maximum rate of relative products elimination is around at 275°C and it is then followed by a steady elimination of volatile products. The rate maximum is due to the accelerated decomposition of the anhydride groups which is confirmed by the spectrum of the polymer heated at this temperature. The decomposition of anhydride is accompanied by continuous weight loss due not only to the eliminated gases (CO, CO_2) but also to chain scission and elimination of products of different volatility which are the constituents of the gas fraction,

liquid fraction and cold ring fraction (tar).

Among the gaseous products, small amount of alkenes and ketene have been identified in addition to CO_2 and CO. In the liquid fraction, the main constituent is acetic acid but some maleic anhydride is also present, both unsubstituted and alkyl substituted. Traces of five membered alkyl substituted lactones are formed. Important products are toluene, cyclic ketones and esters of unsaturated acids. The polymer degrades to high liquid and cold ring fractions (35 and 37% respectively), plus 15% gas fraction and 13% char. The char fraction is quite high compared to PIPAc, ~~and~~ in view of fact that PIPAc has a structure which would favour depolymerisation. The presence of maleic anhydride which has a crosslinking tendency brings about a high char fraction and more stability to thermal degradation than for the homopolymer of poly(isopropenyl acetate). The charred copolymer contains aromatic groups and some anhydride groups survive above 400°C.

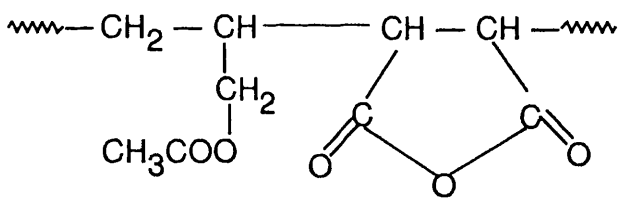
CHAPTER TEN

THE THERMAL DEGRADATION BEHAVIOUR OF THE ALTERNATING COPOLYMER OF MALEIC ANHYDRIDE AND ALLYL ACETATE

INTRODUCTION

The thermal degradation behaviour of the alternating copolymer of maleic anhydride with isopropenyl acetate has been discussed in Chapter 9 and the stability of the above copolymer was compared with that of the isopropenyl acetate homopolymer.

In this Chapter the thermal degradation behaviour of the alternating copolymer of maleic anhydride—allyl acetate (MAn—AllAc) will be discussed.



Both, maleic anhydride and allyl acetate monomers are unlikely to homopolymerise due to their low reactivity. However maleic anhydride can be polymerised through an anionic route (103), while allyl acetate does not polymerise at all due to the steric hindrance of CH_2 group.

Allyl acetate has been the subject of copolymerisation with other monomers (104), but these copolymers have never been subjected to thermal degradation studies.

Table 10.1 The preparation conditions for the alternating copolymer of maleic anhydride and allyl acetate made by free radical polymerisation.

Amount of allyl acetate	61.09 ml (60 g)
Amount of maleic anhydride	9.8 g
Amount of initiator (AIBN)	0.1 %*
Time of polymerisation	8 hours
Temperature of polymerisation	60°C
Conversion	6.5 %

* Relative to the total weight of monomers

The MAn—AllAc copolymer was prepared by free radical polymerisation using AIBN as an initiator. The purification of monomers and the polymerisation methods are described in Chapter 3, while the preparation conditions are listed in Table 10.1.

Most of the thermal degradation studies have been carried out using TVA and TG techniques under programmed heating up to 500°C in nitrogen and vacuum conditions. The thermal degradation in vacuum up to 500°C has also been studied by following the relative rate of volatile product formation in thermal volatilisation analysis experiments with the simultaneous monitoring of the main products by mass spectrometry.

The material balance after pyrolysis has been evaluated. The liquid fraction collected during pyrolysis was analysed by GC-MS, after the removal of the acetic acid formed by pyrolysis. The composition of the liquid fraction was determined by the integration of the ion current under the peaks of the different compounds by GC-MS. The structural changes in the copolymer during degradation investigated at various temperatures up to the point of charring. IR spectroscopy was also used to investigate the isothermal degradation at lower temperatures, 200°C, for various lengths of time under vacuum conditions.

THERMOGRAVIMETRY (TG)

The thermogravimetric (TG) and differential thermogravimetric (DTG) curves for MAn—AllAc copolymer were obtained for degradation under dynamic nitrogen at a heating rate of 10°C/min up to 500°C.

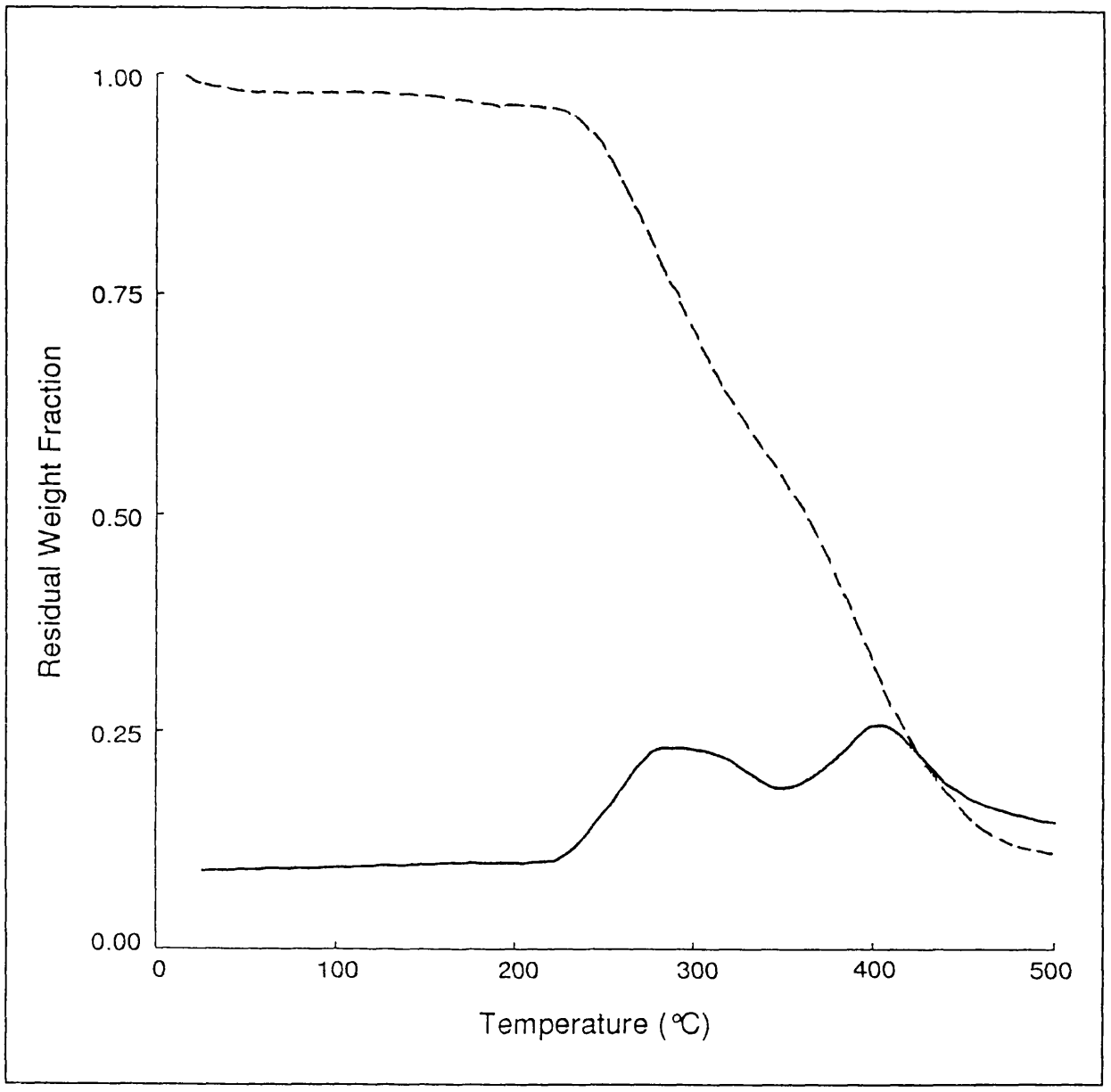


Fig.10.1 TG and DTG curve obtained (heating rate 10°C/min, nitrogen flow) for the MAn—AllAc copolymer

Key : TG ------- DTG ———

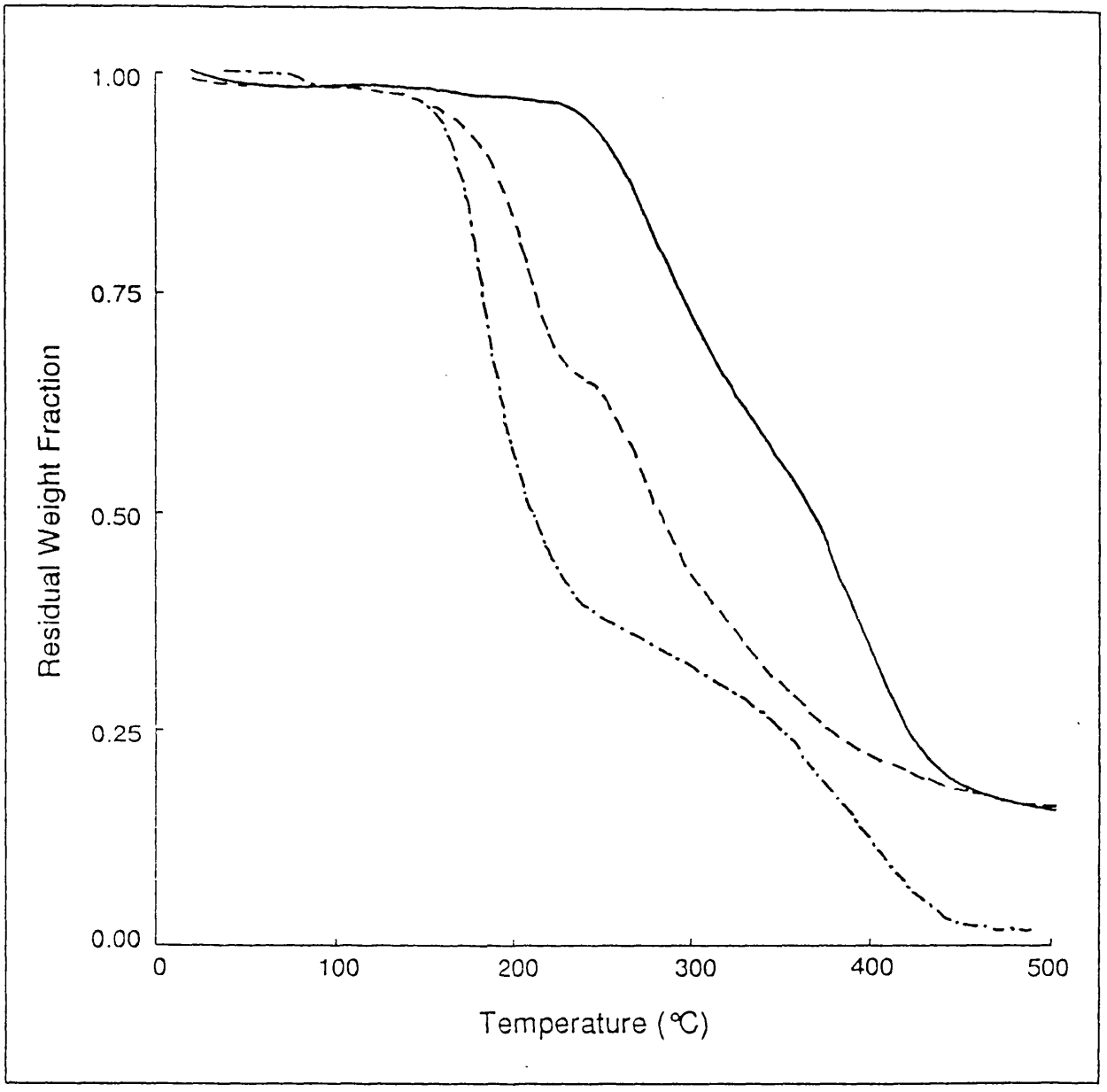


Fig.10.2 TG curves (heating rate 10°C/min, nitrogen flow) for various polymers.

Key : (——) MAn—AllAc copolymer, (------) MAn—IPAc, (- · – · –) PIPAc homopolymer

Table 10.2 TGA data of three polymers degraded under N_2 atmosphere.

% weight loss					
PIPAc		**MAn-IPAc copolymer**		**MAn-AllAc copolymer**	
Temperature region	Wt. Loss	Temperature region	Wt. Loss	Temperature region	Wt. Loss
160-250°C	60	150-250°C	32	200-300°C	22.5
250-350°C	10	250-350°C	34	300-350°C	18
350-475°C	20	350-500°C	18	350-500°C	40
Residue	negligible	Residue	15	Residue	16

PIPAc Poly(isopropenyl acetate)

MAn-IPAc Maleic anhydride—Isopropenyl acetate alternating copolymer

MAn-AllAc Maleic anhydride—Allyl acetate alternating copolymer

The diagram shown in Fig. 10.1 presenting both, the TG and DTG curves shows that the thermal decomposition of the MAn—AllAc copolymer occurs in two main stages. However, the first stage can be further divided into two parts as it will be shown later.

During the first stage, between 225°C and 350°C, an initial weight loss of 22.5% is observed in temperature region 225-300°C, which is followed by more gradual weight loss of 18% up to 350°C. The weight loss of 22.5% corresponds to the volatilisation of carbon dioxide. The IR spectrum of partially degraded copolymer heated up to 320°C shows the partial loss of anhydride rings.

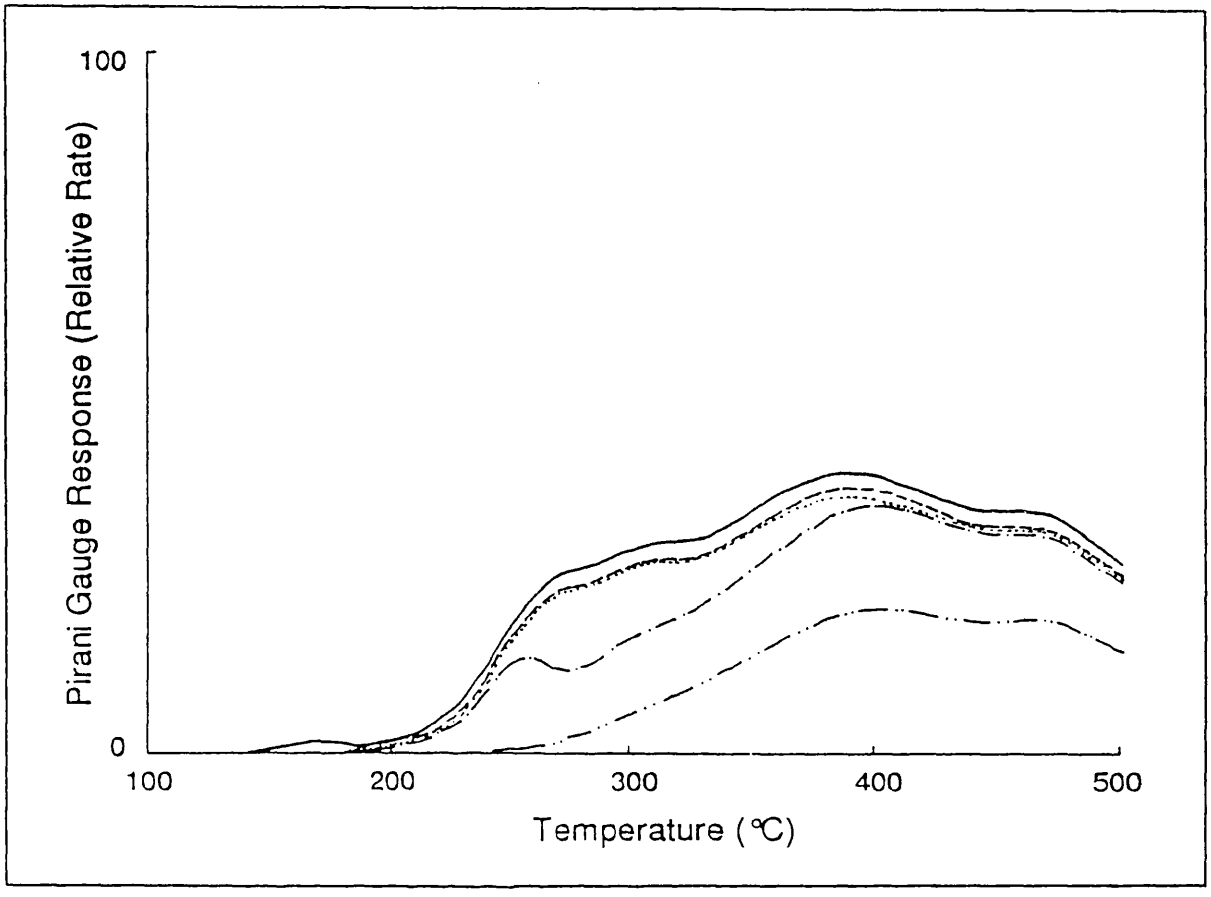
The second stage of decomposition observed in the temperature region 350-500°C, has a rate maximum at 400°C. The weight loss of 40%, occurring in this stage, is probably due to loss of acetate groups followed by gradual breakdown of the residual backbone.

The TG curves are compared in Fig. 10.2 to facilitate the comparison of the thermal resistance of three polymers: poly(isopropenyl acetate), maleic anhydride—isopropenyl acetate copolymer and maleic anhydride—allyl acetate copolymer. The % weight loss for each stage for all three polymers is presented in Table 10. 2.

For MAn-AllAc copolymer heated to 500°C, there is a significant amount of residue (15%) indicated by TG.

THERMAL VOLATILISATION ANALYSIS

The MAn—AllAc copolymer was degraded in a TVA experiment under vacuum using a programmed heating rate of 10°C/min to 500°C.



Key

0℃
-45℃
-75℃
-100℃
-196℃

Fig.10.3 TVA curve for MAn—AllAc copolymer heated in vacuum to 500°C at 10°C/min.

The TVA curve is presented in Fig. 10.3 as the Pirani response reading for the products escaping the -196°, -100°, -75°, -45 and 0°C traps as the temperature increases to 500°C.

The TVA curve is complex, but it shows in general the presence of the two main stages of degradation, the first one from 200 to 350°C and the second 350 to 500°C as observed in TG analysis (Fig. 10.1). The differential condensation of the products in the traps of various temperature indicates the presence of some substages of the main stages.

In a first sub-stage of degradation between 200 and 280°C the material produced can only be condensed at temperatures below -100°C. The maximum rate of decomposition in this stage is around 260°C. The traces corresponding to traps at 0°, -45°, and -75° are almost coincident indicating that the material produced in this temperature region is not condensed by these traps. The temperature region (280-350°C) corresponds to another substage of the first stage. The same considerations apply, except that non-condensable gases begins to form.

In the temperature region 200-280°C, a higher Pirani response for the -100° trap together with direct observation by MS indicate the formation of the expected carbon dioxide. In the temperature region 280-350°C, products of a different nature are evolved: acetic acid and the decomposition products of acetate radicals. Above 300°C, the TVA curve also shows the increasing formation of a non-condensable material at -196°C which is mainly carbon monoxide produced from the breakdown of anhydride rings.

In the second stage of degradation (350-500°C) there are two maxima in the rate of volatilisation, one which is significant around 380°C and a much less well-defined maximum at 470°C.

Table 10.3 TVA and DTG data for MAn—AllAc copolymer

TVA		DTG	
Temp. range °C	T-max °C	Temp. range °C	T-max °C
200-280°C	260°C	225-300°C	270°C
280-330°C	320°C	300-350	320°C
330-440°C	380°C	350-500	405°C
440-500°C	470°C	____	____

Table 10.4 The material balance of the fraction collected during the degradation to 500°C of the alternating copolymer of allyl acetate and maleic anhydride in a TVA experiment.

No	Fraction	%
1	Condensable liquid of which	41.5
1*a*	O-containing compounds	32.86
1*b*	Aromatic compound	37.35
1*c*	Aliphatic compounds	3.1
1*d*	Other	26.69
	Total	100
2	Cold ring fraction	24
3	Residue	16
4	Non-condensable (by difference)	18.5

The trace for the gases escaping the -196°C trap shows the presence of the two maxima and is quite high indicating there is a large fraction of non-condensable material produced in this temperature region.

Above 400°C the residual chain is extensively fragmented and products of small volatility are formed. T-onset, and T-max for the copolymer in the TVA and TG curves are summarised in Table 10.3.

At the end of the experiment the fractions of compounds of different volatility were collected and were determined quantitatively by direct weighing. The results are presented in Table 10.4. The major fraction consists of condensable gases and liquids (41.5%). This is followed by the cold ring fraction (24%), non-condensable gases (18.5%) and residue (16%). The non-condensable gases are calculated by difference.

The TVA curve (Fig. 10.2) suggested that the products evolved in the early stage of degradation are highly volatile, such as CO_2. Some non-condensables (CO) were also present. To confirm the above another set of experiments, in a closed system, was carried out. For this purpose, a relatively small size of sample (10 mg) was taken into a twin limbed degradation tube, which had one limb attached to an IR gas cell. The tube was evacuated to 10^{-4} torr and sealed off under vacuum. The part of the tube containing the sample was placed in an oven and heated at 200°C for 30 minutes. During this time, the gases were condensed into the IR cell using a liquid nitrogen trap. The gas cell was then isolated from the main tube and examined by IR spectroscopy showing the presence of CO_2 and a small quantity of CO.

THE EVOLUTION OF THE INDIVIDUAL DEGRADATION PRODUCTS

The degradation of the MAn—AllAc copolymer in vacuum has also been followed by monitoring by mass spectroscopy the formation of main degradation products, while recording the relative rate of volatile product formation according to the procedure of thermal volatilisation analysis (TVA).

The evolution of the individual products was followed by plotting the intensity of the lines produced in the mass spectra by their characteristic ions versus temperature. The evolution of CO_2 was followed through its characteristic ion (m/e = 44) and that of acetic acid through its ion at m/e = 60 and it is shown in Fig. 10.4a. It is evident from the figure that CO_2 begins to evolve around 200°C and continues up to 500°C. The acetic acid begins to evolve much later than the CO_2, at around 260°C. This is consistent with the results presented by the TVA experiment (Fig. 10.3).

Fig. 10.4b shows the formation of furanone and 2-butenal -2-methyl, through the lines 55 and 84. However m/e 55 can also be contributed by other products e.g. crotonaldehyde, 2-methyl propenoic acid. The formation of 2,3-dihydro-3-(1-methyl propyl) furanone, m/e 69 and 98, is shown in Fig. 10.4c. These products are all formed in minor quantities in the temperature region (250-350°C) and almost entirely between 350 and 450°C. This is also true for the main product identified in the liquid fraction, 2-methyl cyclopent^{2}ene-1-one, (Fig. 10.4d, m/e 67 and 96).

Most of the aromatic compounds are formed only in the second stage of degradation, except toluene which begins to form earlier at 320°C. Fig. 10.4e shows the formation of toluene, xylene and trimethyl benzene, through their characteristic ions (m/e = 91, 105 and 120 respectively).

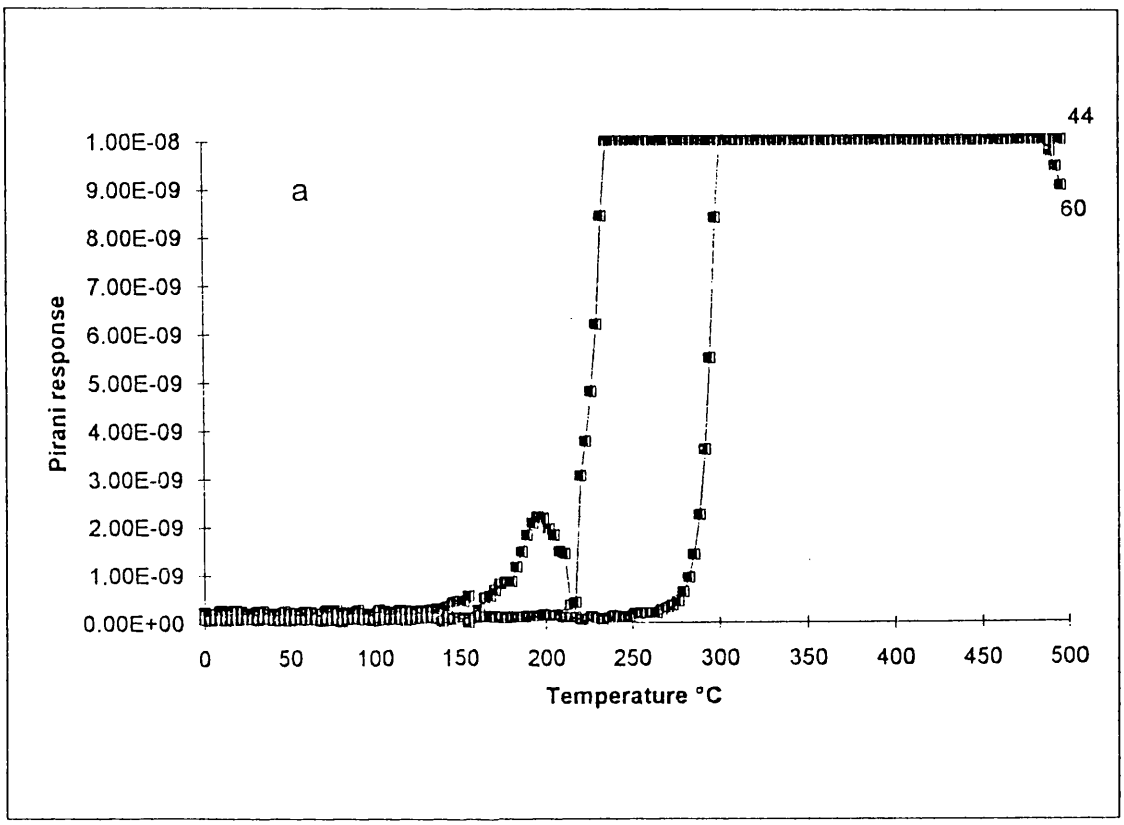


Fig.10.4 The formation pattern of main degradation products of MAn—AllAc copolymer (Heating rate 10°C/min up to 500°C) under TVA conditions

a: The formation of CO_2 through (m/e = 44) and acetic acid through (m/e = 60)

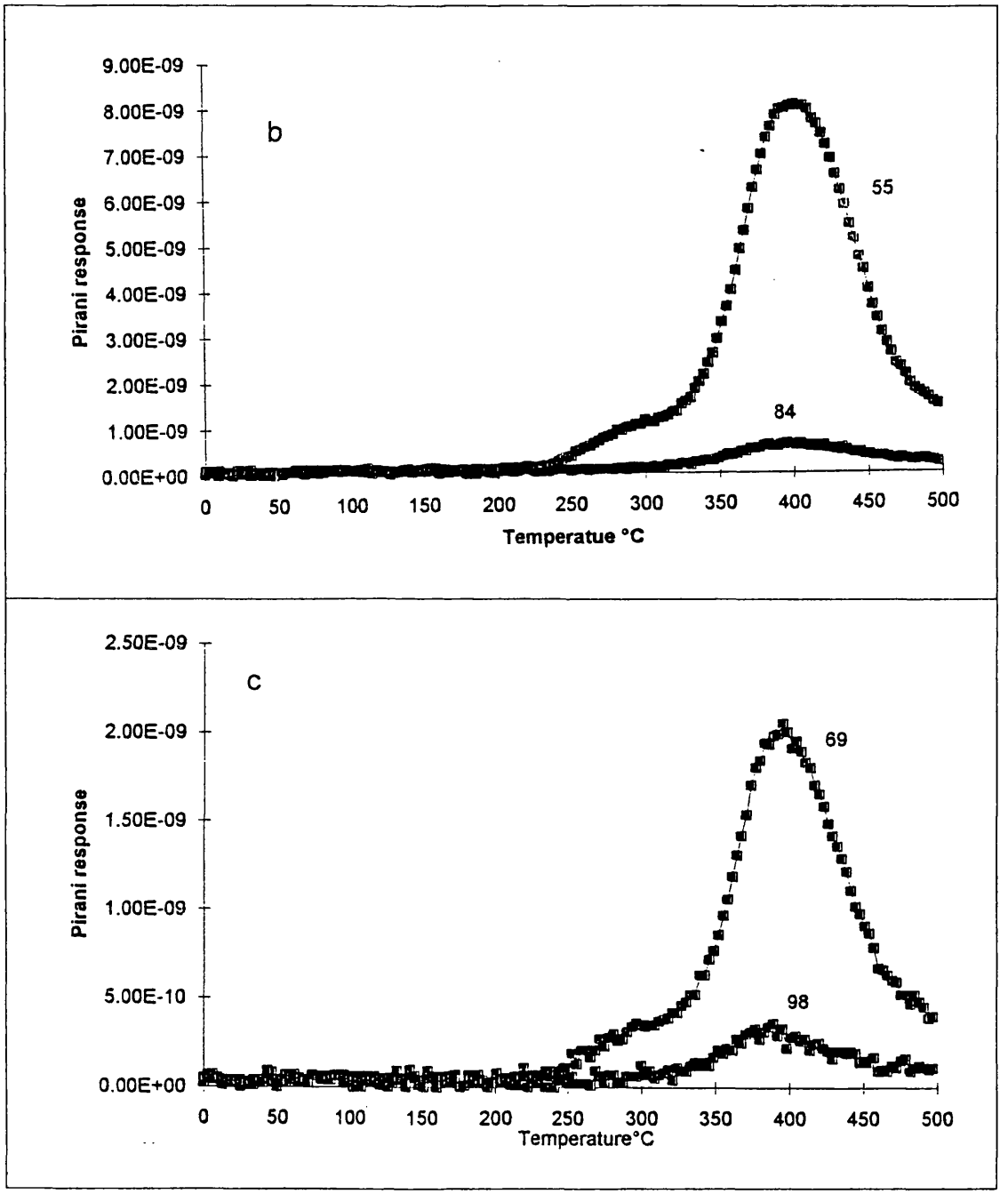


Fig. 10.4 Continued

b: Formation of 2-butenal 2-methyl furanone through (m/e = 55 and 84)

c: Formation of 2,3-dihydro-3-(1-methyl propyl) furanone through (m/e = 69 and 98)

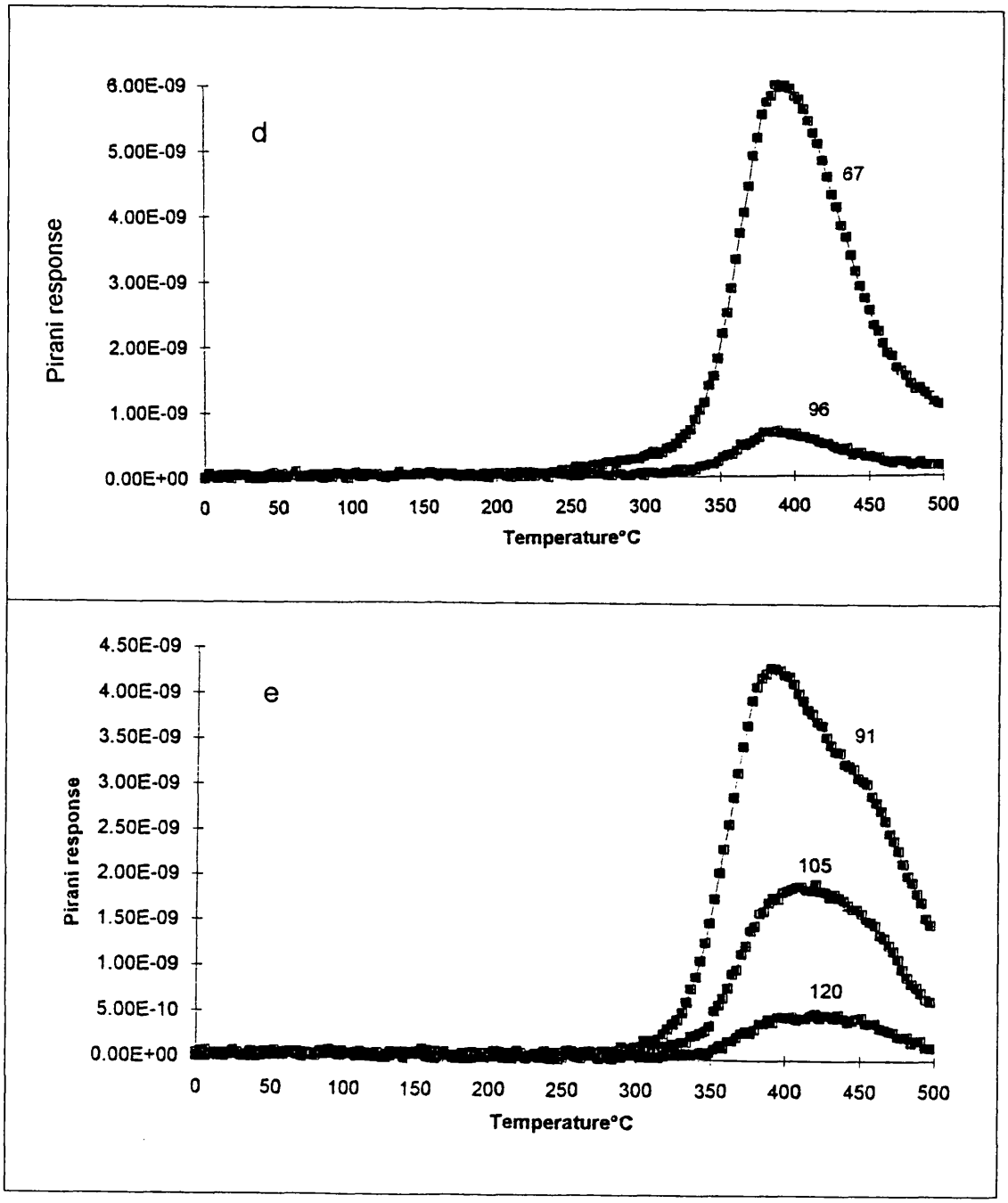


Fig. 10.4 Continued

d: Formation of 2- methyl cyclopent-2-ene-1-one, through (m/e = 67 and 96)

e: Formation of toluene, xylene and trimethyl benzene through (m/e = 91, 105 and 120)

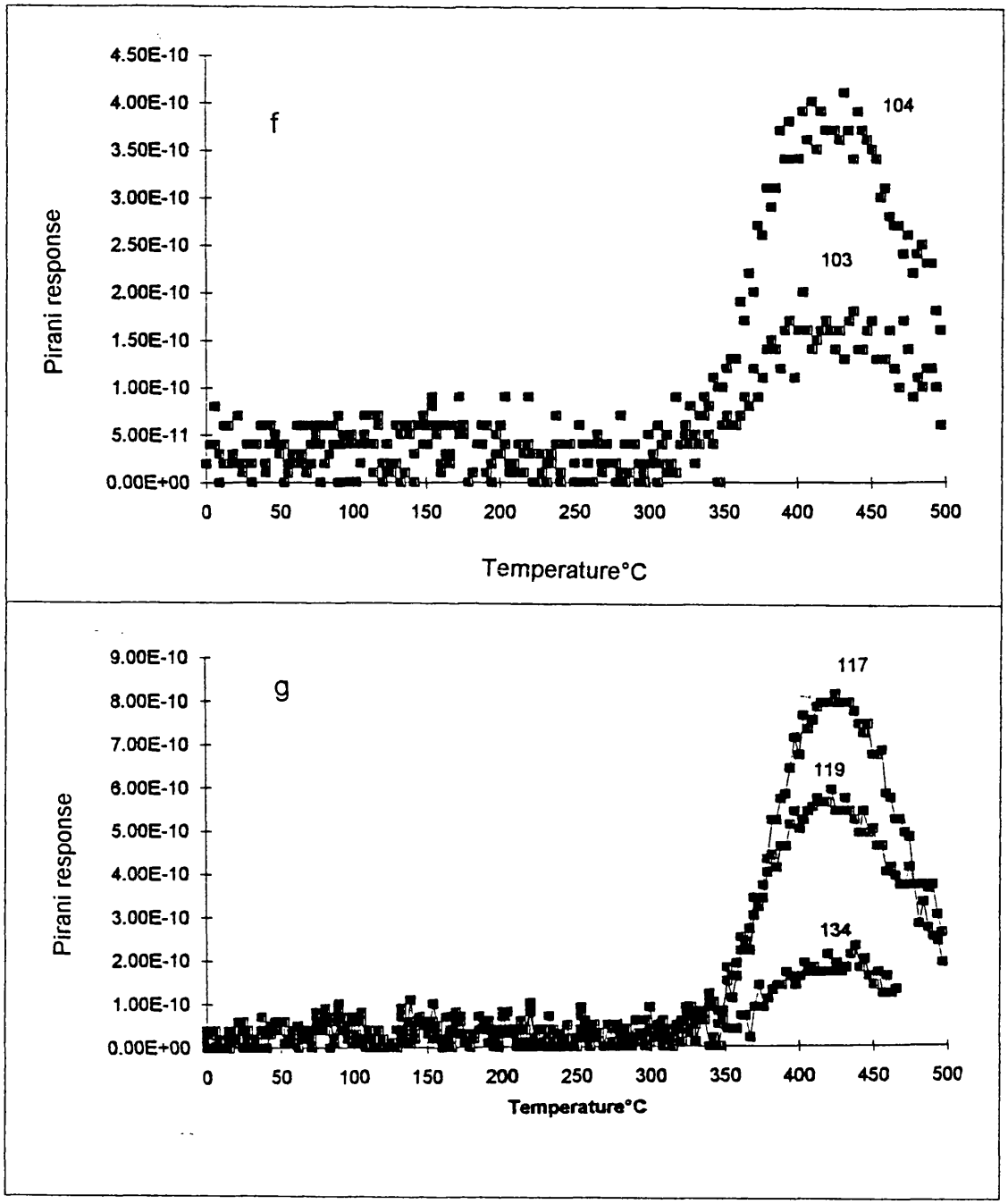


Fig. 10.4 Continued

f: Formation of ethenyl benzene through (m/e = 104 and 103)

g: Formation of dimethyl ethyl benzene through (m/e = 117 and 134) and dimethyl ethenyl benzene through (m/e = 119)

The formation of ethenylbenzene is shown in (Fig. 10.4f) through its characteristic ions of m/e 104 and 103. The curve is noisy due to the small quantities in which this compound is formed, however, the trends in the intensity are clear. Alkyl substituted dimethyl ethyl benzene are plotted through the lines at m/e 117 and 134 and dimethyl ethenyl benzene (line 119) are shown in Fig. 10.4g. The curves show the same trend, the compounds being formed mainly in the second stage of degradation.

Non-condensable products are also formed. The main product is carbon monoxide together with a small amount of methane and hydrogen. The non-condensable fraction, of which the main product is CO, mainly forms in the temperature region (300-500°C).

SUBAMBIENT THERMAL VOLATILISATION ANALYSIS

The condensable gases and liquids collected during the degradation of the polymer in the TVA system were separated into their components by the SATVA method. Mass spectroscopic analysis was carried out during the SATVA separation by bleeding the products into the mass spectrometer coupled to the TVA system. The condensable gases were also analysed by IR spectroscopy.

The SATVA curve presented in Fig. 10.5 shows four peaks. The first peak, of very small magnitude, is due to some aliphatic hydrocarbons. The second peak is due to large quantities of CO_2 and can be seen through the broad absorption bands: stretching, ν at 2340, 3700 cm^{-1} and bending (∂) at 670 $cm.^{-1}$ The intensity of these absorptions emphasises the large volume of CO_2 present. The peaks 3a and 3b, which are not well resolved, are mainly due to acetic acid, ν (C=O) at 1740 cm^{-1}, however, small amounts of ketene and water have also been identified.

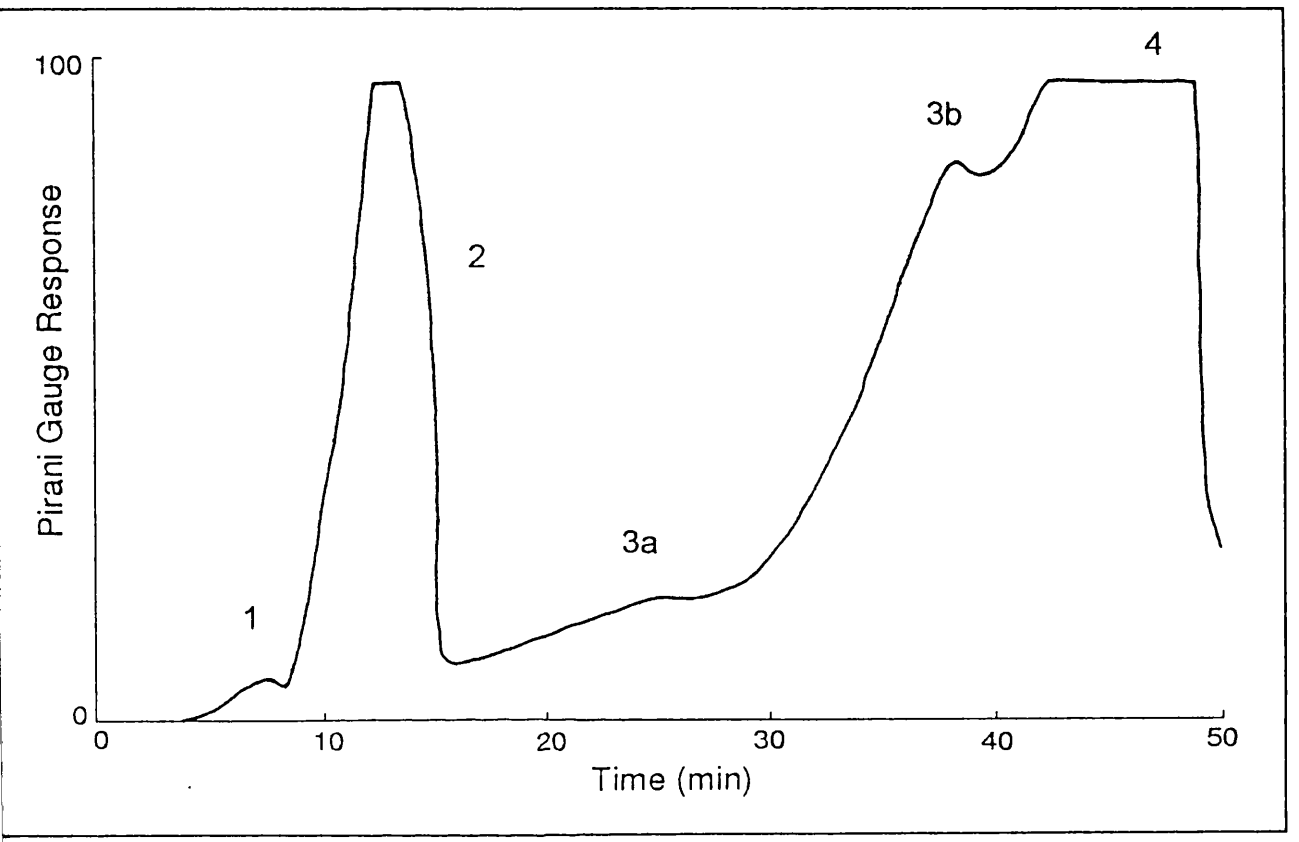


Fig.10.5 SATVA curve of the degradation products, obtained under TVA conditions of MAn—AllAc copolymer.

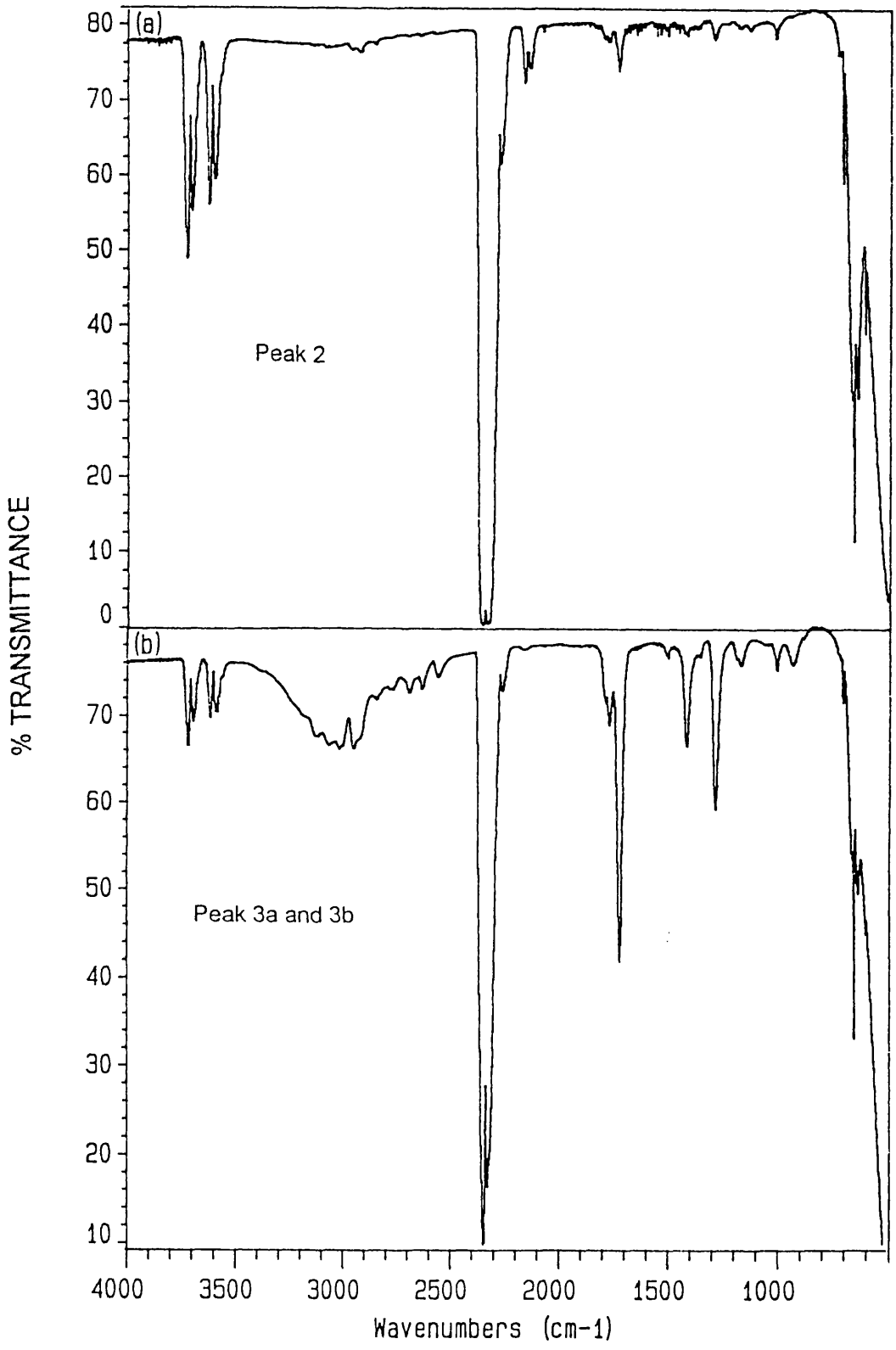


Fig.10.6 Infrared spectra of the condensable gases and liquid fraction for degradation of MAn—AllAc copolymer to 500°C under TVA conditions.

Table 10. 5. Products of the thermal degradation of MAn—AllAc copolymer to 500°C at 10°C/min, under vacuum established by the listed methods.

Noncondensable at -196°	Condensable volatile Gases	Liq. Fraction	Cold ring fraction	Residue
MS only	IR & MS		IR MS & GC-MS	IR only
CO CH_4 hydrogen	CO_2 ethene propene ketene	acetic acid propenoic acid butyrolactone toluene, xylene trimethylbenzene	anhydride and lactones, decomposition products condensed and substituted aromatic rings	black involatile α,β-unsaturated ketones, decomposed lactones, heavily fused and substituted aromatic rings

Table. 10. 6 The composition of the liquid fraction collected during the pyrolysis of Maleic anhydride and Allyl acetate copolymer

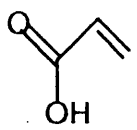
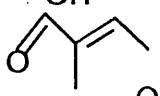
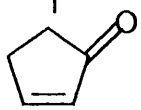
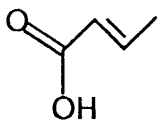
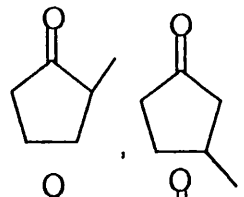
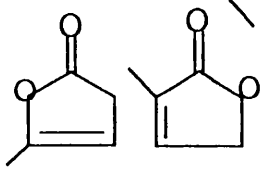
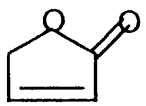
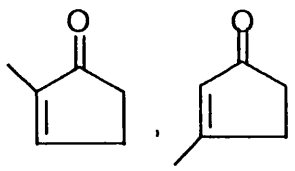
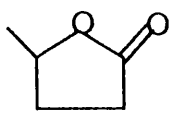
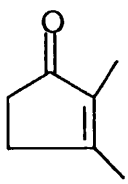
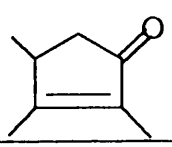
Compound Oxygen Containg		MW	%
1		72	3·3
2		84	2·8
3		84	1·3
4		86	0·80
5		98	5·8
6		98	2·0
7		84	1·9
8		96	7·2
9		100	2·4
10		110	4·6
11		124	0·7
Total O- Containing Compounds		——	33

Table 10.6. Continued

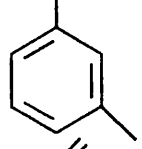
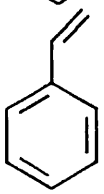
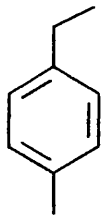
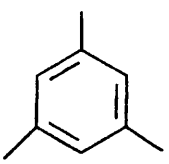
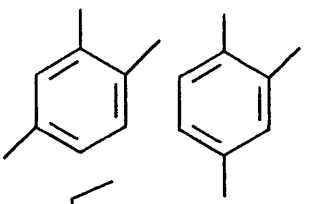
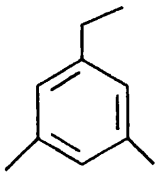
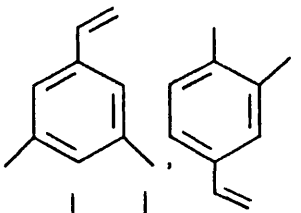
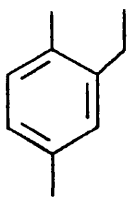
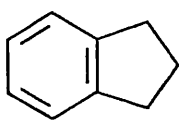
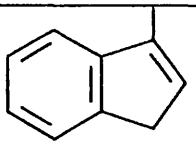
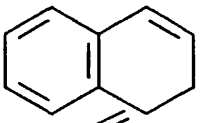
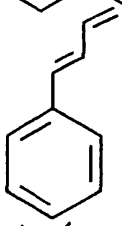
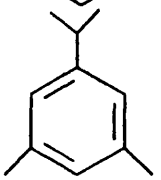
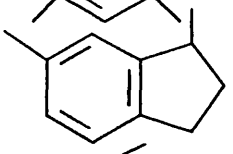
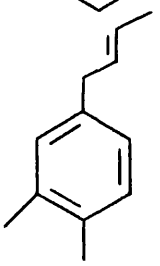
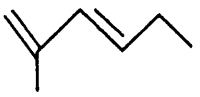
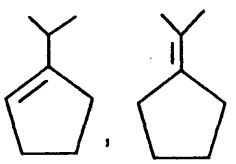
Aromatic Hydrocarbon	MW	%
12 	92	4·0
13 	106	5·7
14 	104	3·1
15 	120	1·3
16 	120	3·1
17 	120	0·62
18 	134	2·0
19 	132	1·8
20 	134	4·5
21 	132	2·40

Table 10.6 Continued

Aromatic compounds	MW	%
22 	130	2·3
23 	130	2·24
24 	130	2·0
25 	148	1·33
26 	146	0·6
27 	160	0·29
Total aromatic	——	36
Aliphatic Hydrocarbon		
28 	96	1·3
30 	110	1·81
Total Aliphatics	——	3·11
Others	——	28
Total General	——	100

The IR spectra for the products at peak 2 and peaks 3a-b are presented in Fig. 10.6(a-b).

Table 10.5 shows the products identified in the various degradation fractions. In the case of the liquid fraction, only the volatile products which were identified by IR spectroscopy and on-line mass spectrometry are listed. The liquid fraction collected during the TVA experiment was also examined by the GC-MS technique after removing the acetic acid which is the major product in fraction. The GC-MS chromatogram shows a variety of important and trace products which are listed in Table 10.6. As it can be seen the important products in liquid fraction are methyl substituted cyclopentenones (8 and 10), the saturated homologues (5) and C2, C3 and C4 alkyl and alkenyl benzenes.

THE COLD RING FRACTION

The infrared spectrum of the dark brown cold ring fraction (CRF) collected during the degradation of the MAn—AllAc copolymer to 500°C is presented in Fig. 10.8b. The CRF was collected from the TVA tube for quantitative determination using a suitable solvent and transferred to a weighed bottle. After evaporation of the solvent at room temperature, the weight of the cold ring fraction was determined. The CRF was examined by IR spectroscopy and by mass spectrometry using a probe heated to different temperatures. It was also analysed by GC—MS.

The CRF, amounting to 24% of the initial weight of the copolymer, is mostly formed in the second stage of degradation. In a separate experiment, the polymer sample was heated up to 350°C under TVA conditions and it was found that an insignificant amount of CRF had been formed.

Table 10.7. Assignment of the major peaks in the IR spectrum of the undegraded MAn—AllAc copolymer.

Band (cm^{-1})	Assignment
2970	CH_3 asymmetric (C—H) stretch
2930	CH_2 asymmetric (C—H) stretch
2870	CH_3 symmetric (C—H) stretch
1854 &1794	C=O stretch of anhydride ring
1750	C=O stretch of ester group
1460	CH_2 bending deformation
1440	CH_3 asymmetric bending
1370	CH_3 symmetric bending
1250	(C—O—C) symmetric stretching
1170	(C—O—C) symmetric stretching
1035	(CH—O) symmetric stretching
940	(C—CH_3) rocking
735, 605	(O—CO) bending and other deformations

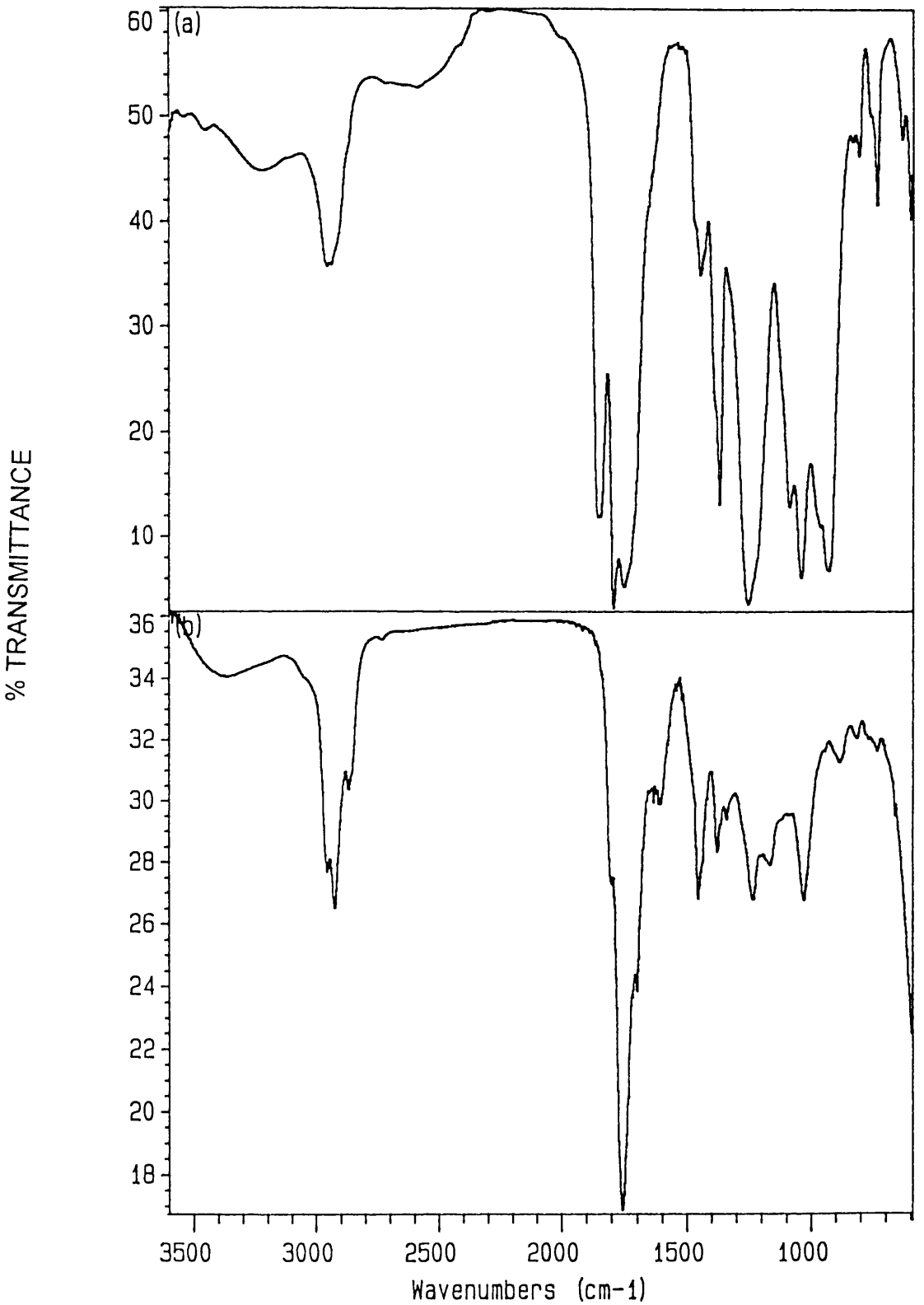


Fig.10.8 IR spectra of (a) undegraded copolymer (b) cold ring fraction of MAn—AllAc copolymer to degraded to 500°C under TVA conditions.

Table. 10.8 The composition of the cold ring fraction (CRF) collected during the pyrolysis of MAn—AllAc copolymer (products are listed according to their relative abundance)

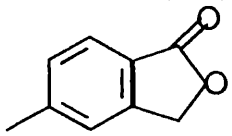
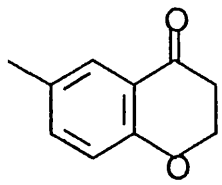
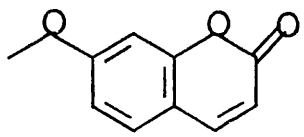
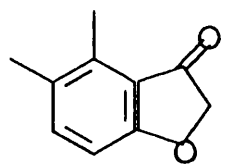
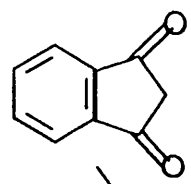
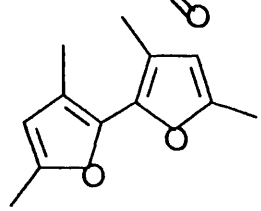
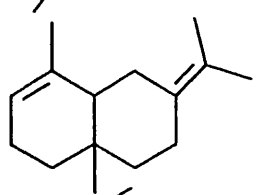
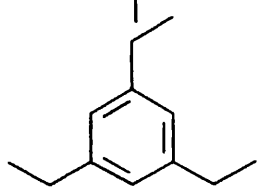
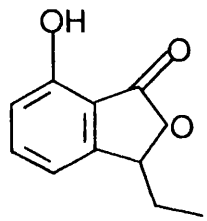
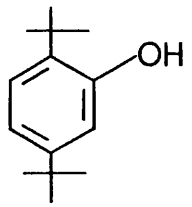
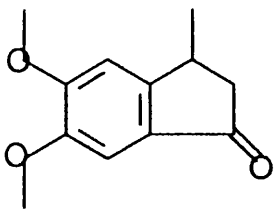
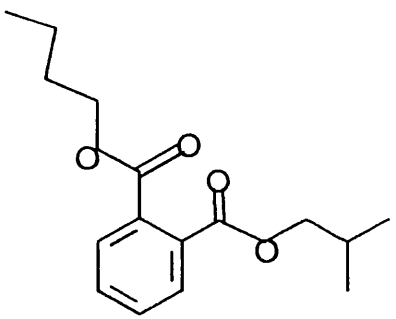
	Compound	MW
1		148
2		162
3		162
4		176
5		176
6		190
7		204
8		165
9		178

Table 10.8 Continued

Compound	MW
10 	206
11 	206
12 	278

This also demonstrates that in the first stage of degradation (200-350°C) the products evolved are of a higher volatility.

The IR spectrum of the undegraded copolymer is also presented for comparison in Fig. 10.8a. The assignments of the main absorption peaks of the undegraded MAn—AllAc copolymer are presented in Table 10.7.

The main features of CRF spectrum are the anhydride bands present at 1808 and 1766 cm.$^{-1}$ These carbonyl absorptions of the anhydride ring were present in the original copolymer at 1854 and 1794 cm^{-1} but they are shifted to a lower wavenumber in the CRF of the degraded copolymer. The absorption at 1808 cm^{-1} (weak) indicates that the anhydride is unsaturated. An absorption at 1766 cm^{-1} shows the presence also of lactone groups in the CRF.

The IR spectrum shows a relatively small aromatic content. A small shoulder at 3030 cm^{-1} and the absorption at 1604 cm^{-1} show the presence of aromatic rings. The substitution pattern of the aromatic rings cannot be seen in the finger print region due to the cut-off of the NaCl plate. The band at 890 cm^{-1} which is relatively important can be attributed to the out of plane bending of one or two C—H bonds or to the vinylidene type unsaturation present in the system.

A significant band due to conjugated double bonds is present at 1652 cm^{-1}. An absorption of small intensity can also be seen at 1703 cm^{-1} which is attributable to the α, β-unsaturated ketones (C=O). The α,β-unsaturated ketones have also been observed in the CRF of MAn—IPAc copolymer discussed in Chapter 9. The CRF spectrum shows no trace of ester groups, contrasting with the CRF of MAn—IPAc copolymer where ester groups are prolific.

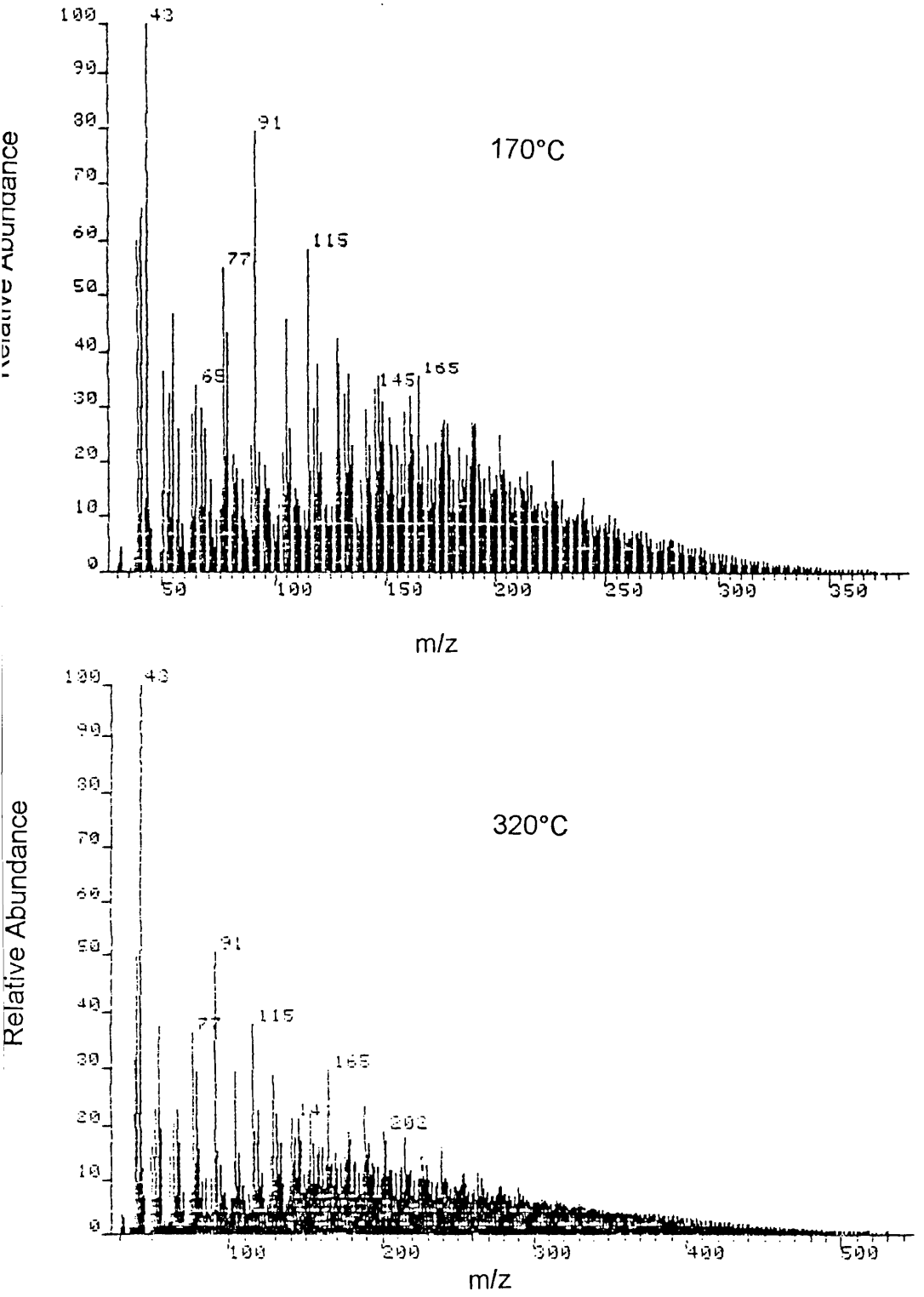


Fig.10.9 Mass spectrometric results of cold ring fraction (CRF) from the degradation of MAn—AllAc copolymer to 500°C under TVA conditions.

This indicates that in the case of MAn—AllAc copolymer the CRF is only produced at higher temperatures, long after the acetic acid has been eliminated, whilst in the MAn—IPAc copolymer CRF is formed throughout heating, before and during acetic acid elimination, hence acetate groups are incorporated in the large scission fragments constituting CRF.

The cold ring fraction was also examined by mass spectrometry using probe heated to 170 and 320°C which gave a complex spectrum (Fig. 10.9a-b) indicating a mixture of material of molecular weight up to 500.

The CRF was also examined by GC-MS techniques, the identified products being listed according to their relative abundance in Table 10.8.

POLYMERIC RESIDUE

The black involatile residue obtained from the MAn—AllAc copolymer after degradation under TVA conditions up to 500°C was analysed by IR spectroscopy. The mass of residue left after the TVA experiment was 16% of the original polymer and is in good agreement to the % residue observed in TG analysis.

The IR spectrum of the residue is presented in Fig. 10.10b, while the spectrum of the original copolymer is presented in Fig. 10.10a for comparison. The spectrum shows that some anhydride groups have survived up to 500°C as can be seen through C=O absorptions present at 1805 and 1762 $cm.^{-1}$ The intensity of the anhydride absorptions is slightly greater than observed in the CRF spectrum.

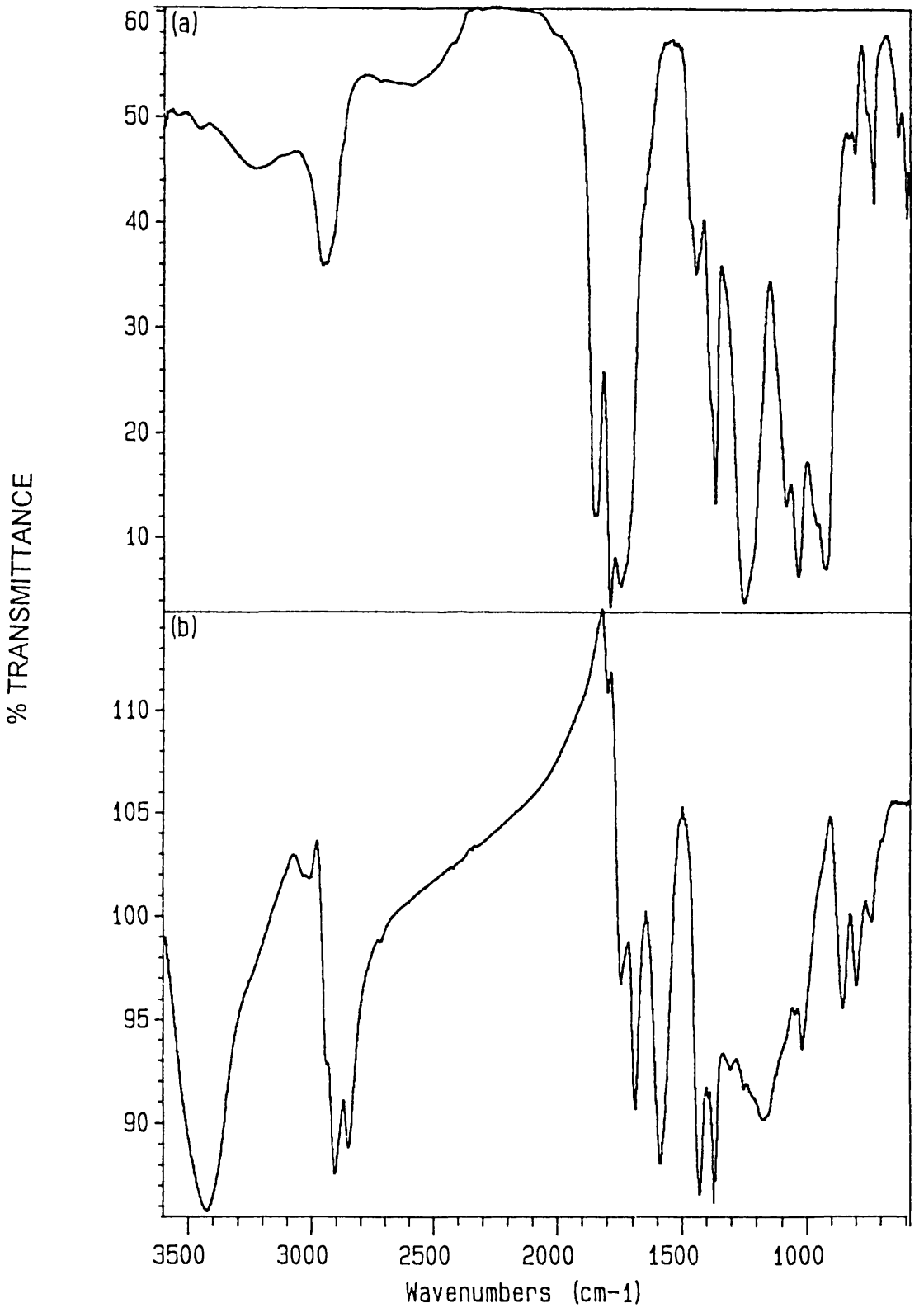


Fig.10.10 IR spectra of (a) undegraded copolymer (b) residual fraction of MAn-AllAc copolymer degraded to 500°C under TVA conditions.

The carbonyl absorption at 1701 cm^{-1} is attributable to the α, β-unsaturated ketone groups formed on the aliphatic hydrocarbon chain. This C=O absorption which has also been observed in CRF spectrum as a shoulder is strong in the residue indicating that more ketone groups are formed as a result of the decomposition of anhydride rings.

Another feature of the spectrum of the polymeric residue is the strong aromatic content. The aromatic content can be seen through the absorptions at 3030 and 1450 $cm.^{-1}$ The aromatic content is also evident through the substitution pattern in the fingerprint region which show the out of plane bending of four and five C—H groups (748 cm^{-1}), three C—H groups (810 cm^{-1}) and one and two C—H groups at (880 cm^{-1}). The broad OH absorption is due to the free water condensed during KBr disc formation.

In the case of poly(isopropenyl acetate), it decomposes completely around at 400°C leaving a negligible amount of residue. In the cases of MAn—IPAc and MAn—AllAc copolymers a significant amount of residue is observed after 500°C. This is probably due to the development of crosslinking and condensation of aromatic rings which considerably enhances the stability of the residual polymer.

FTIR-SPECTROSCOPIC INVESTIGATION OF STRUCTURAL CHANGES DURING THE DEGRADATION OF MAn—AllAc COPOLYMER

The structural changes in the MAn—AllAc copolymer during thermal degradation have been investigated by FTIR reflection absorption spectroscopy using a film cast on a stainless steel high reflection plate.

A film sample of polymer was cast on the stainless steel plate as follows. Firstly, a saturated solution of 5 mg of polymer in acetone was uniformly spread on a steel plate. The acetone was allowed to evaporate at room temperature. The apparently dried film was then kept in vacuum oven at 40°C for 48 hrs and finally heated at 100°C for 20 minutes to evaporate any trace of solvent.

Typically, in a temperature programmed experiment the changes in polymer structure were followed by heating the polymer film at a rate of 10°C/min to different temperatures up to the point of char. The heated film was then cooled rapidly with fan assistance at a rate of approximately 50°C/min. FTIR spectra were measured using reflection-absorption apparatus. In some cases a diffuse reflectance spectrum was obtained, in which case the spectra were subjected to automatic deconvolution.

The structural changes upon heating at temperatures from 200 to 480°C are illustrated in Fig. 10.11(b-g). The main absorption bands of the undegraded copolymer spectrum (Fig. 10.11a) are presented in Table. 10.7.

The polymer sample heated up to 200°C (Fig. 10.11b) does not show any significant change in structure. Upon heating up to 240°C the spectrum (Fig. 10.11c), shows a noticeable change in the C=O absorption of the anhydride

bands. The intensity of the C=O absorption for anhydride rings present at 1854 cm^{-1} has decreased, indicating the beginning of the degradation of anhydride groups at this temperature. The polymer heated to 280°C shows extensive decrease in the intensities of the C=O absorptions of anhydride region (Fig. 10.11d). The absorption at 1854 cm^{-1} is reduced and left as a shoulder. The C=O absorption of the ester initially present at 1750 cm^{-1} is also reduced but very little with respect to the anhydride band at 1794 cm^{-1}. The FTIR spectrum confirms the TVA results (Fig. 10.3) that the only volatile product in the region 200-280°C is CO_2. The weight loss of 22% also confirms this. The newly appeared band at 1653 cm^{-1} (small) is due to the formation of conjugation of double bonds in polymer backbone.

At 320°C, the C=O absorption at 1854 cm^{-1} has disappeared completely as can be seen in Fig. 10.11e. The carbonyl absorption present at 1794 cm^{-1} is now shifted to a lower wavenumuber, 1768 $cm.^{-1}$ This and the newly appeared band at 1170 cm^{-1} indicate the formation of a different species of carbonyl group. The band at 1768 cm^{-1} could be attributed to lactone formation in the polymer chain. The number of methyl substituted lactone-type products identified in the liquid fraction also supports the lactone formation in the system (Table 10.6). The C=O absorption of the ester groups has been considerably reduced, in fact it is barely noticeable. If it is present in any concentration at all it might be masked by the overlapping of the broad absorption band of C=O at 1768 $cm.^{-1}$ There are changes in the relative intensity of the 1448 (δ_a CH_2), 1370 (δ_s CH_3) and 1240 (υ_s C—O—C) cm^{-1} showing the loss of acetate groups. The δ CH_2 band initially present as a shoulder at 1460 cm^{-1} has disappeared indicating that CH_2 groups suffer transformations as well. The band at 1653 cm^{-1} for internal unsaturation is fully developed now, indicating more unsaturation (double bonds) in the system. It is difficult to make any assignment regarding the nature of the unsaturation. However, on basis of the small band which appears at 920 $cm,^{-1}$ chain end (vinyl type) unsaturation is possible. Early signs of

aromatisation developing in the system are present as shown by changes in the finger print region attributable to the substitution in aromatic rings. The new weak band at 1604 cm^{-1} also shows the beginning of aromatisation in the system.

When heated to 400°C the polymer shows significant changes (Fig. 10.11f). The lactone rings formed at lower temperature are beginning to decompose as indicated by the relative ratio of the alkyl (2970 cm^{-1}) and lactone C=O (1768 cm^{-1}) bands. The TVA curve shows a large fraction of non-condensables (mainly CO) produced around at 400°C due to the breakdown of the lactone rings. The new band at 1703 cm^{-1} is indicative for α,β-ketones embedded in the unsaturated backbone. The α,β-unsaturated ketones are also identified in the IR spectrum of the polymeric residue. A strong aromatic content through increased intensity of the absorption bands at 1604 and 1450 cm^{-1} and the out of plane bending in the fingerprint region (which are usually strong bands below 900 cm^{-1}) can be documented. The out of plane bending bands can be conveniently identified according to the number of adjacent hydrogen atoms on the phenyl groups. The spectrum of the polymer heated to 400°C shows all types of substitution of the aromatic ring through C–H out of plane bending of five H atoms (750 cm^{-1}), four H atoms (780 cm^{-1}), two and three (820 cm^{-1}) and one H (890 cm^{-1}). The band at 890 cm^{-1} can also be attributed to vinylidene type end chain unsaturation.

When the polymer is heated up to 440 and 480°C, the spectra (Fig. 10.11g-h) present the features of a charred polymer. The C=C absorption at 1653 cm^{-1} is diminished and the absorption band at 1604 cm^{-1} is enormously increased indicating a large aromatic system, both strongly substituted and condensed. An important feature of the polymer heated to 480°C, is the enormous increase in intensity of absorption at 1703 cm^{-1} indicating the increase of ketone groups which are conjugated with the unsaturated backbone.

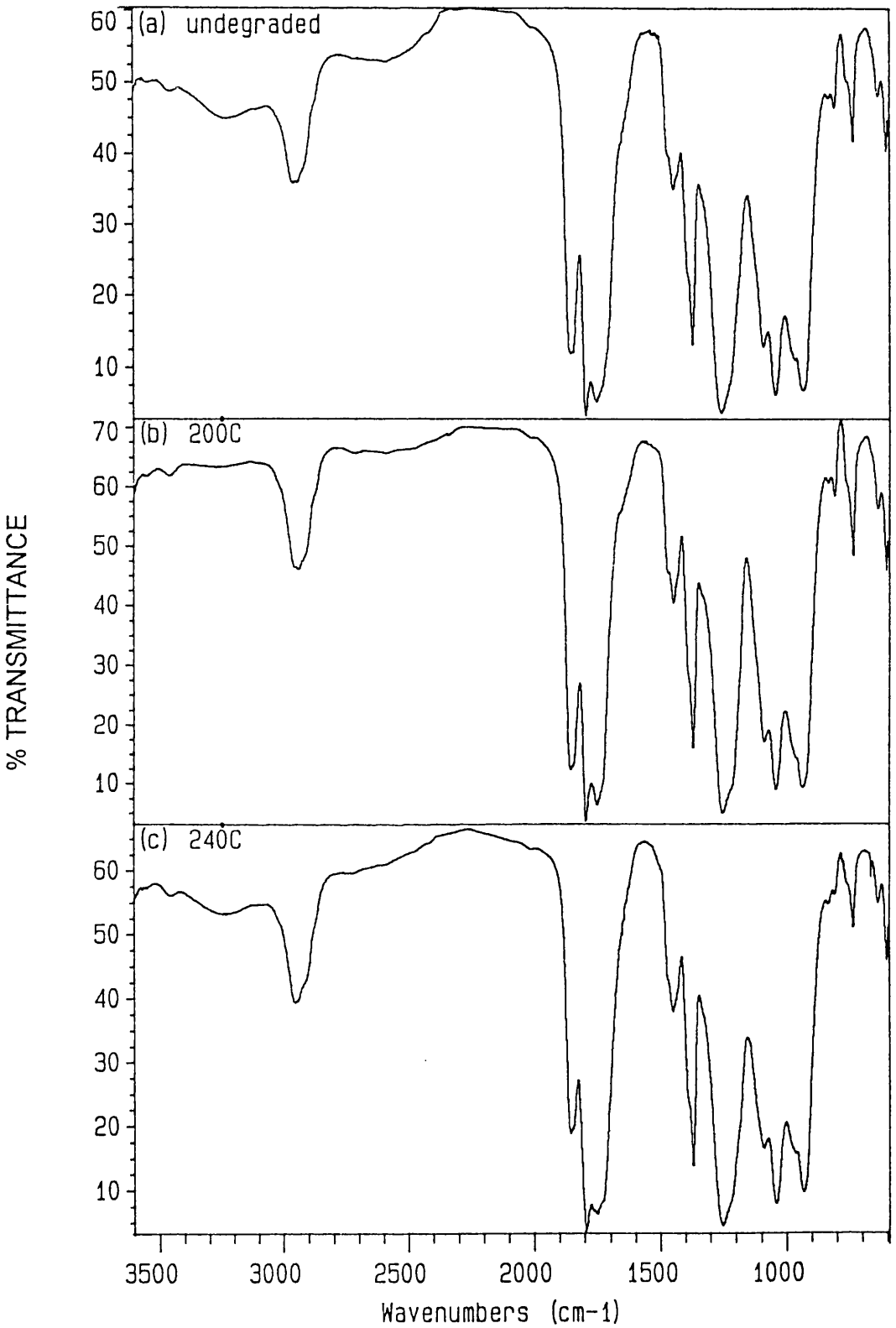


Fig.10.11 Infrared spectra of the MAn—AllAc copolymer : (a) before and after heating in vacuum to : (b) 200°C, (c) 240°C.

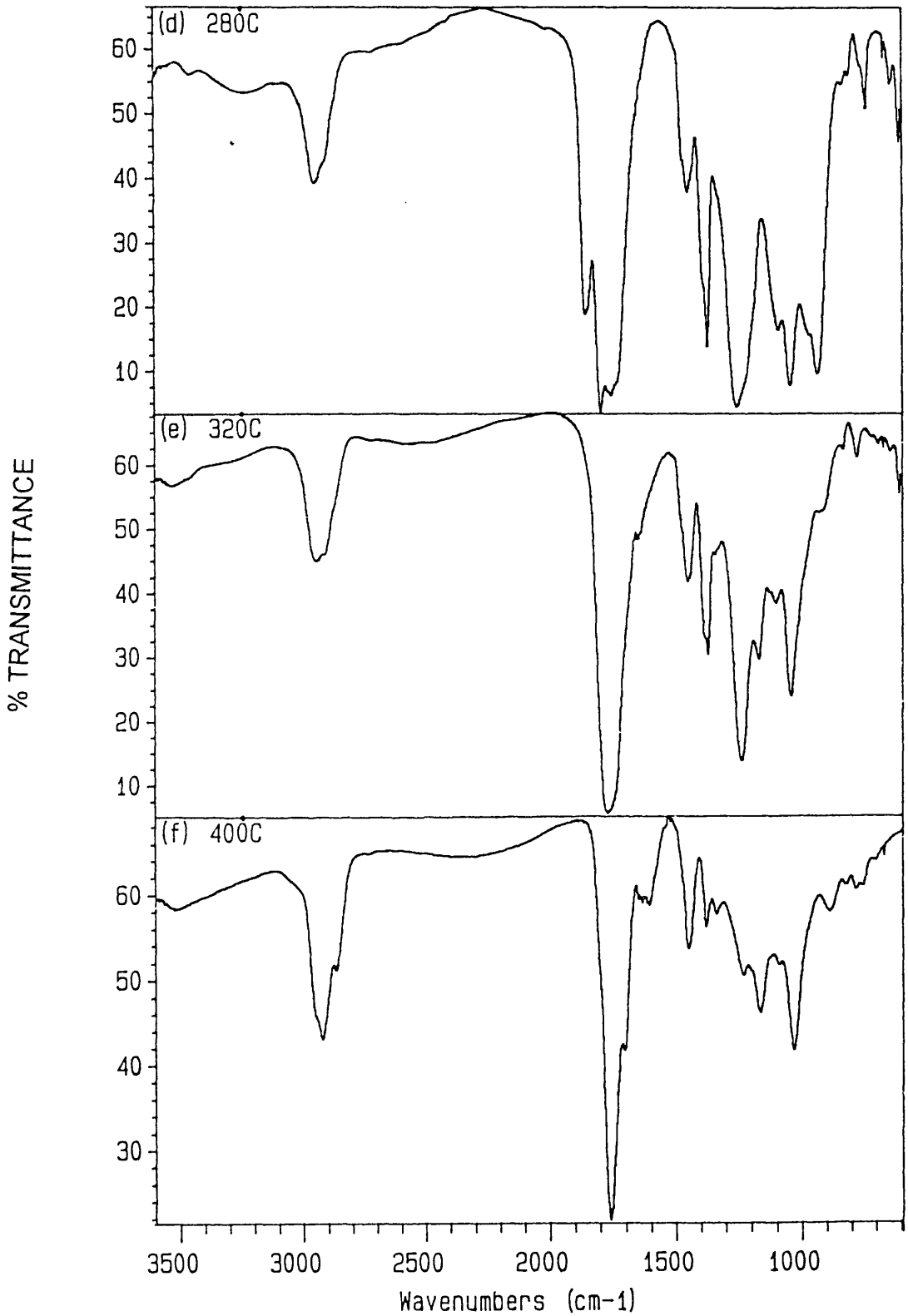


Fig.10.11 Continued (d) 280°C, (e) 320°C, (f) 400°C.

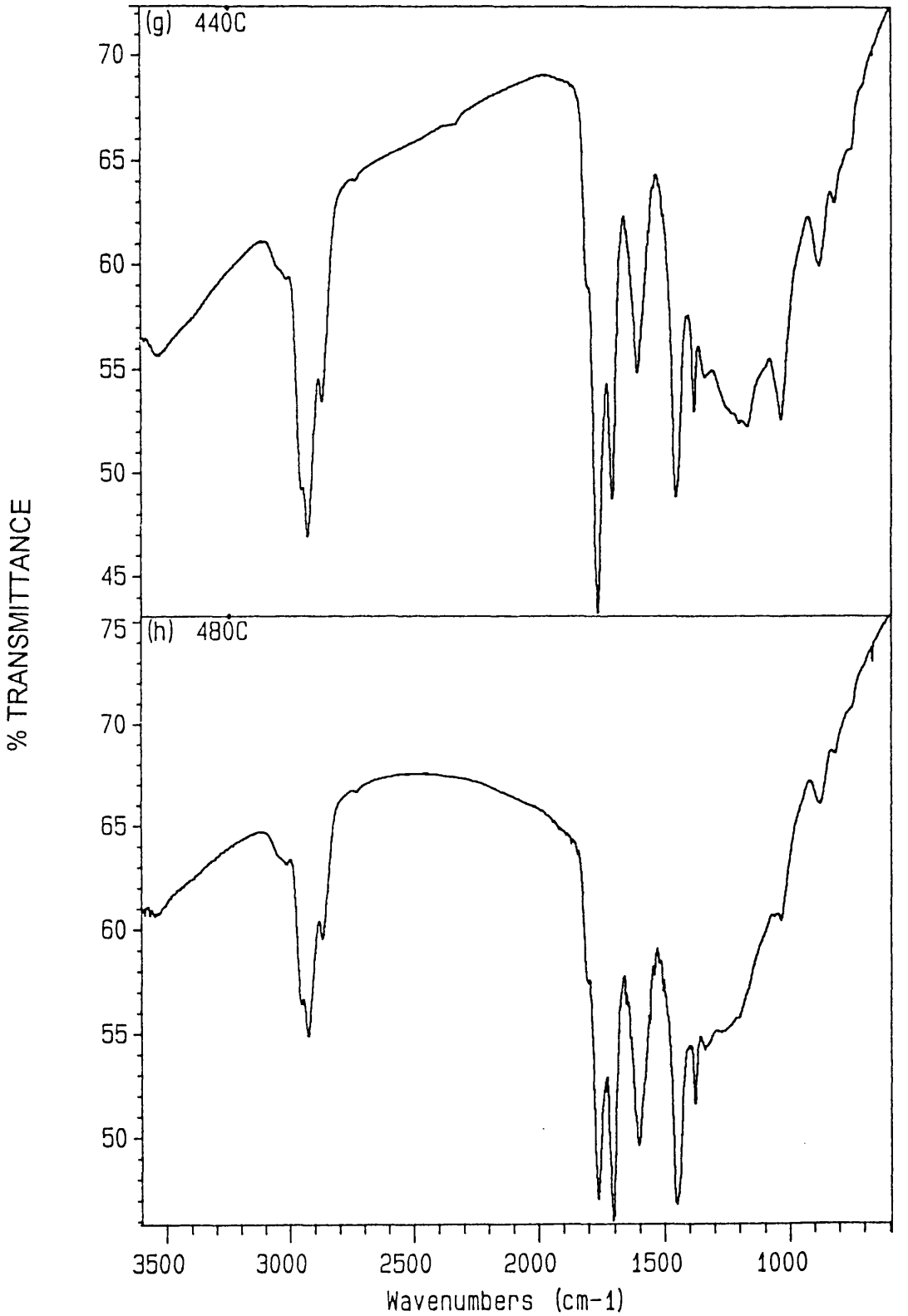


Fig.10.11 Continued (g) 440°C, (h) 480°C.

The spectrum shows the presence of some lactone groups (1764 and 1170 cm^{-1}) which have survived at this temperature.

ISOTHERMAL DEGRADATION AT LOWER TEMPERATURE

In order to confirm the above FTIR findings isothermal experiments were also carried out on MAn—AllAc copolymer at lower temperatures. A film was cast on a stainless steel plate then dried using the same method as described previously. The supported sample was heated in the degradation tube at 200°C under vacuum for various length of time, cooled down to room temperature and the spectroscopic changes at different times of heating were recorded by FTIR.

The spectroscopic changes with a time heating at 200°C from 10 minutes to 6 hrs are presented in Fig. 10.12(b-g). The spectrum of undegraded copolymer is presented in Fig. 10.12a. On heating the polymer at 200°C for 10 and 20 minutes the spectra show only a decrease in intensity at 1854 cm^{-1} indicating the decomposition of some anhydride rings (Fig. 10.12b-c).

Further decrease in the intensity of the C=O absorption at 1854 cm^{-1} can be observed in the spectrum of the polymer heated for 60 minutes, at which stage this absorption is now left as a shoulder. The carbonyl absorption of anhydride at 1794 cm^{-1} has also decreased and it is now less intense than that of the ester group. There is no change in the ester group absorption observed up to this period. The decrease in the C=O absorptions of the anhydride group suggests that the decarboxylation process begins at 200°C, while the acetate groups are quite stable at this temperature.

The spectra of the polymer heated for 100, 240 and 360 minutes are presented in Figs. 10.12, e, f and g, respectively.

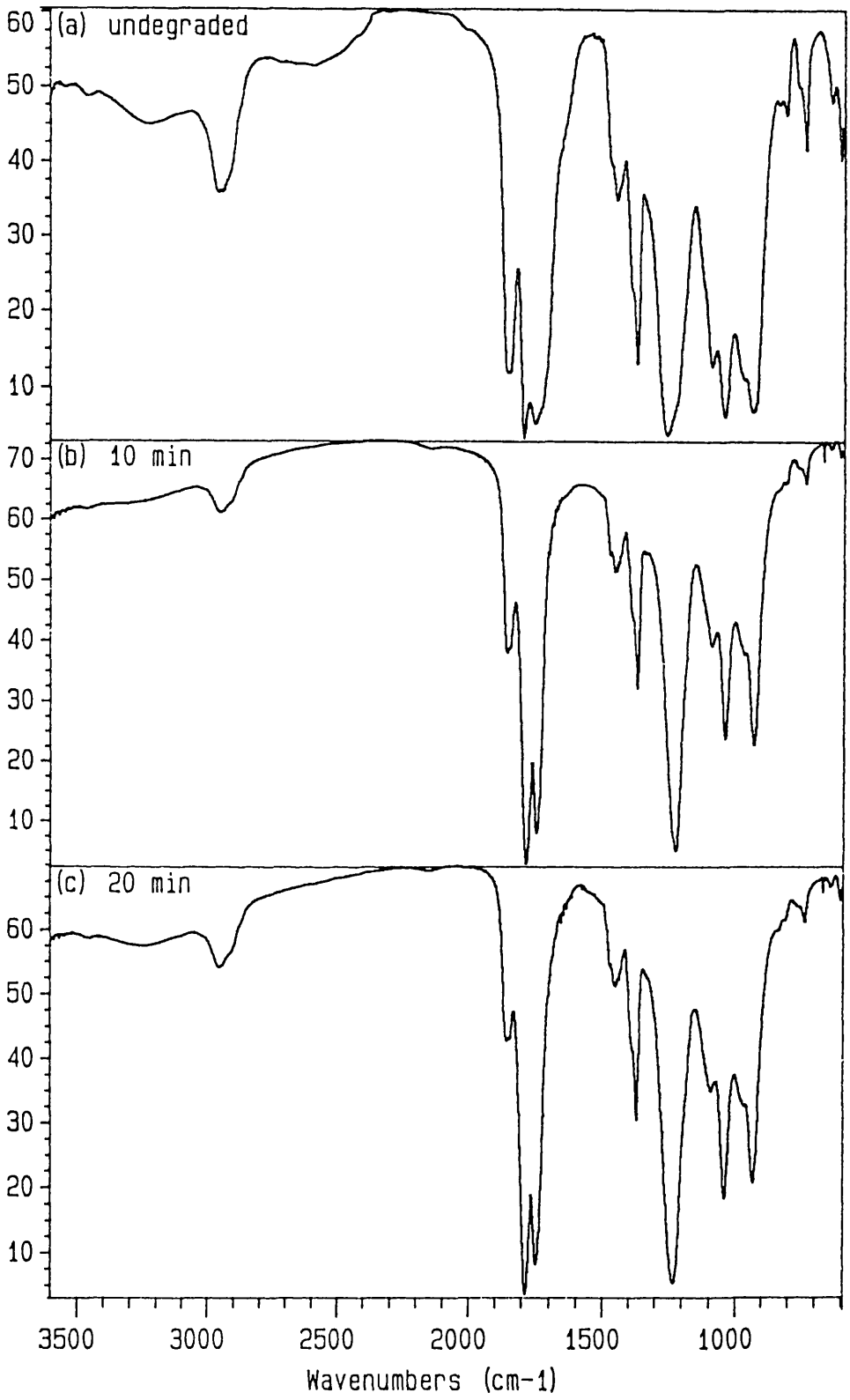


Fig.10.12 Infrared spectra of the MAn—AllAc copolymer : (a) before and (b) — (g) after heating in vacuum for various times.

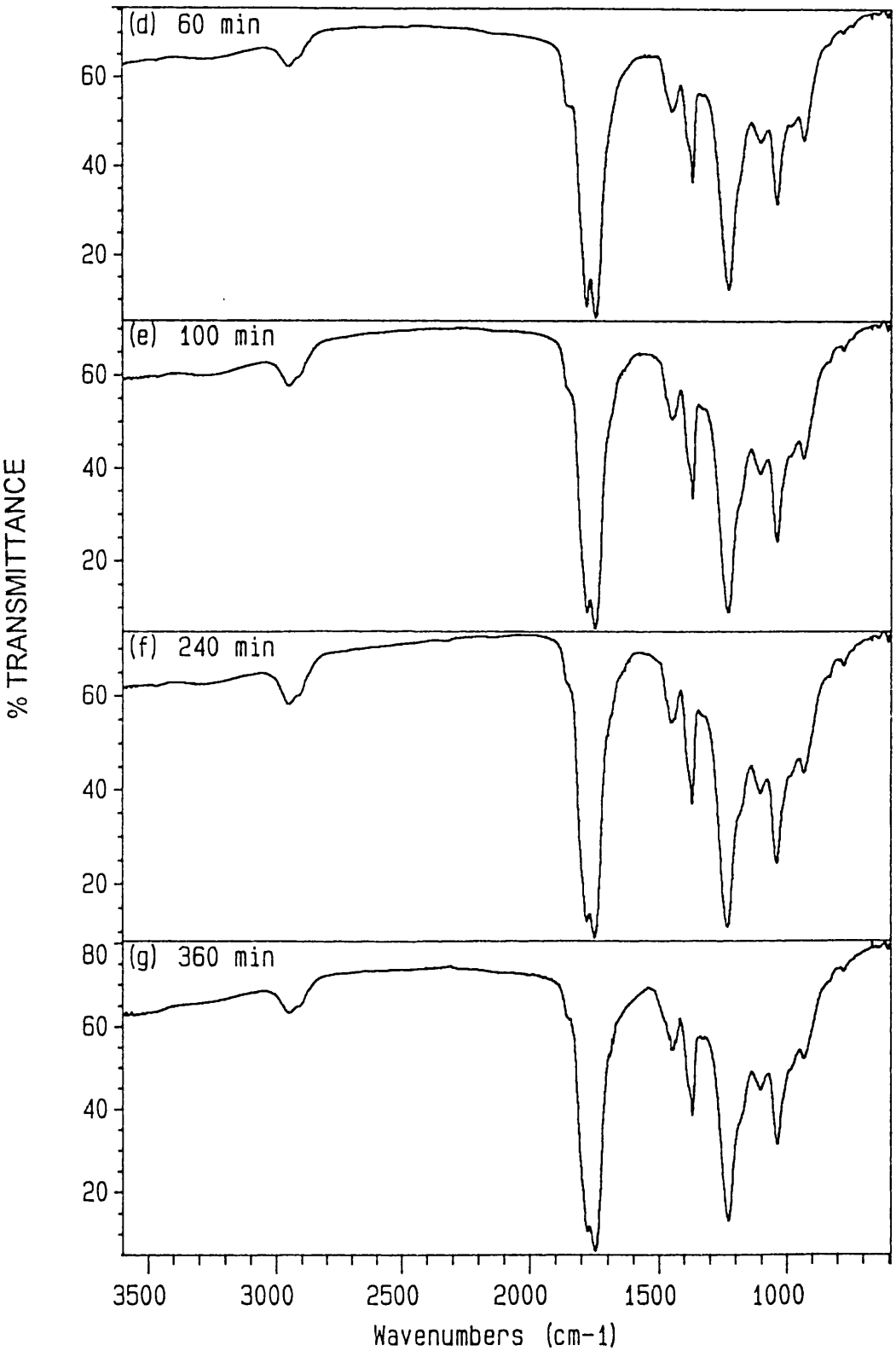


Fig.10.12 Continued.

The spectra show further decrease in the intensity of the absorption at 1854 cm^{-1} with the time of heating. After heating for 360 minutes the band is barely noticeable. The absorption at 1794 cm^{-1} has also decreased markedly, being left as a shoulder after 6 hrs of heating. A very minute band at 1653 cm^{-1} can also be seen in the spectrum of the polymer heated for 6 hrs indicating the appearance of unsaturation in the system. At high degradation time (> 100 min) the loss of some acetate groups can be noted by the disappearance of C — CH_3 rocking band (1940 cm^{-1}) and O - CO deformation bands at 735 and 605 cm^{-1}, although this is difficult to appreciate from the main bands associated to the acetate group.

For the MAn—AllAc copolymer the intensities of the C=O absorption bands for the anhydride demonstrate that the decarboxylation process begins earlier than the deacetylation. This confirms the TVA result (Fig. 10.3) that products condensed in the -100° trap in the temperature region (200-280°C) result from the volatilisation of CO_2 from the polymer chain. In contrast, for MAn—IPAc copolymer, discussed in Chapter 9, the deacetylation process begins earlier than the decarboxylation. This is also the case with MAn—VA copolymer (33).

DISCUSSION

The experimental data presented above show that the chemical transformations of the polymeric backbone depend very much on the temperature.

Between 200 and 280°C, CO_2 is the main product. Around 250°C CO is also formed. The FTIR spectrum indicates a slight content of unsaturation around this temperature. The decomposition of some of the anhydride groups (reaction 1, Scheme 1a) is the source of these products and induces

the formation of double bonds in the polymer. In the temperature region 280-350°C acetic acid is the main product. The FTIR spectra show that in this temperature region there is loss of acetate groups, further decomposition of anhydride groups, the appearance of a new species, the lactone, and an increase in unsaturation (double bond) in the polymer.

These transformation are summarised in Scheme 1a and 1b as follows. The loss of acetate groups through acetic acid elimination involves the loss of H atom at the tertiary C atom with the formation of pendent vinylidene groups (structure I) through reaction (2). The acetic acid elimination is through a 6 membered intermediate involving the H bound to the C atom situated in β to the ester group (91). Reaction (3) (Scheme 1b) shows the decomposition of an anhydride group next to the pendant vinylidene group, structure (III) is the polymer structure created by the loss of some acetate groups. The decomposition of the anhydride groups in this environment eliminating CO creates biradical (IV) (reaction 3). In biradical (IV) the —CO—O• radical attack the pendent vinylidene group closing the ring to a γ-lactone still bearing a biradical (V) (reaction 4).

Biradical (V) can have H transferred from other positions to have a radical site satisfied or can establish double bonds if H transfer is not effective. Reaction (5) considers one possibility. Through reaction (5) one radical site establishes a double bond and the H atom in excess is transferred from 4 carbons distance to satisfy the remaining radical site. The γ-lactone having structure (VI) is expected to absorb at 1770 cm^{-1} in IR. Alternatively, the double bond can be established inside the lactone ring and the second radical site can be either satisfied by H transfer (structure VII) or can form a double bond (structure VIII). The unsaturated lactones (VII) and (VIII) are expected to have absorptions towards lower wavenumbers: 1750 cm^{-1} and below (100) which have not been observed. Other possible structures with double bonds out side the lactone ring (IX and X) are expected to have IR

absorptions at 1770 cm^{-1} as long as the double bond is not in the α position to the C=O group. Structure (XI) with the double bond out side the lactone ring but in α position to the C=O group is expected to have IR absorption at 1720 cm^{-1} which has not been observed. Hence, the most possible lactone structures are (VI), (IX) and (X).

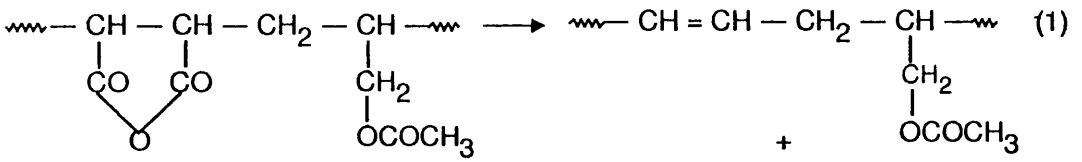
The lactone group can be formed in an opposite direction where a CH_2 group separates the lactone from the pendant vinylidene group. In case of δ lactone (6-membered rings) which usually give absorptions at 1735 and 1720 cm^{-1}, respectively, which have not been observed. Moreover, the pyrolysis products identified in Table 10.6 show the formation of 5 membered lactones and not 6 membered ones.

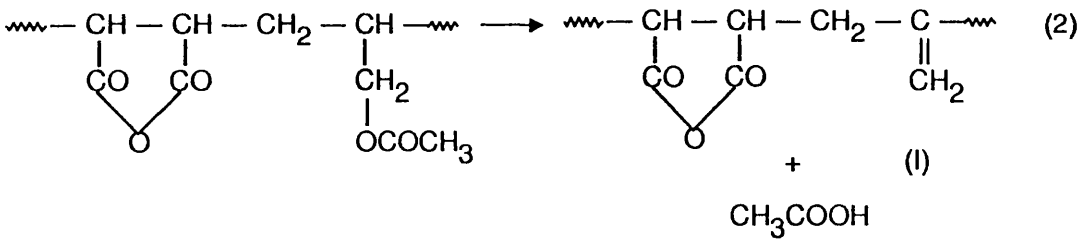
Scheme 2a, reaction (6) shows the generic formation of γ-lactone pyrolysis products by scission from the polymeric backbone. Products number 3,6,9 in table 10.7 have similar structure.

Scheme 2b shows the formation of cyclopentenone type products, also encountered in Table 10.6. The decomposition of the anhydride group with CO_2 elimination and the loss of CH_3COOH from ester groups (reaction 7) create a carbonyl radical in the vicinity of a pendant vinylidene group. The reaction (8) between the two groups closes ring, (XII), having a nearby radical site. Rearrangement (reaction 9, 10) and scission (reaction 11, 12) lead to product (XIII), similar to products numbers 5, 8, 10 11 in Table 10.6.

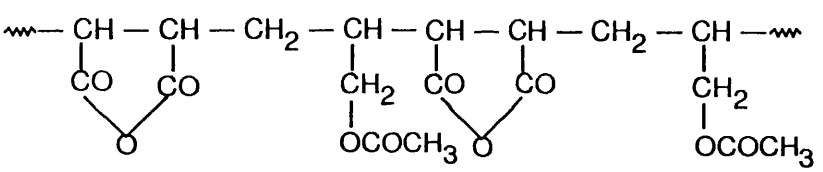
Mechanism of Degradation for Maleic Anhydride - Allyl Acetate Copolymer

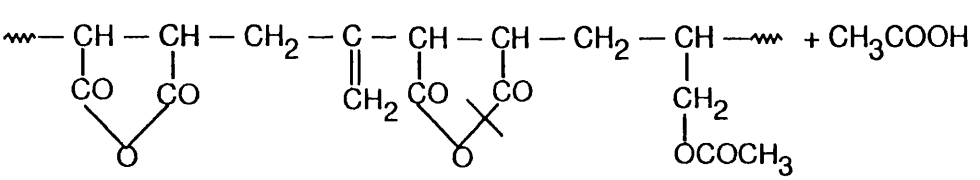
SCHEME 1a



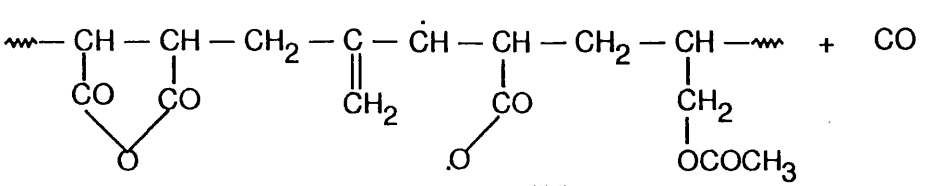


SCHEME 1b



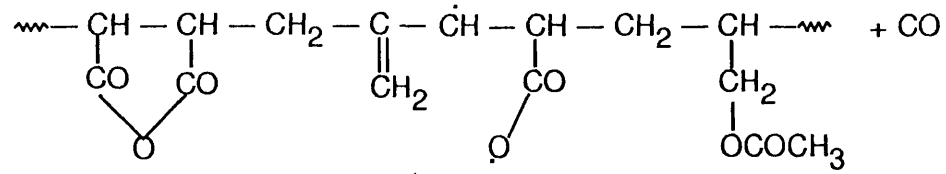


(III)

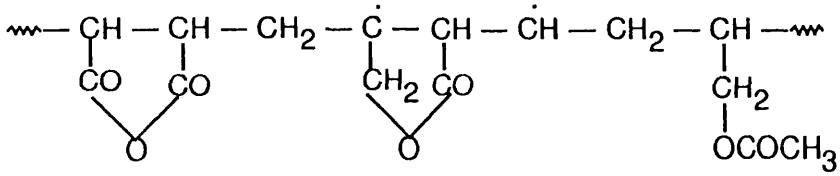


(IV)

SCHEME 1b Continued

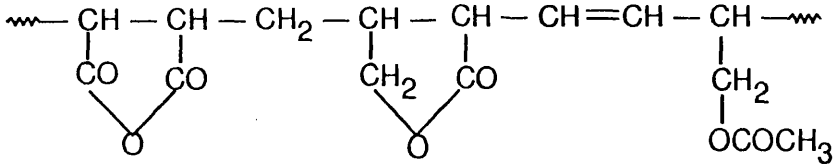


H shift and
ring clouser



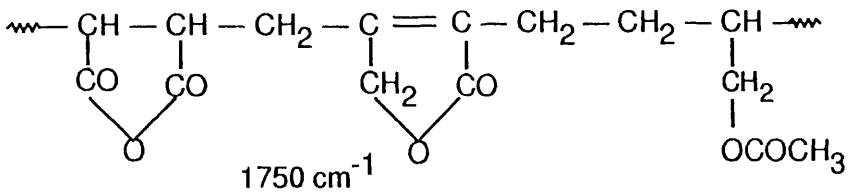
(4)

(V)



(5)

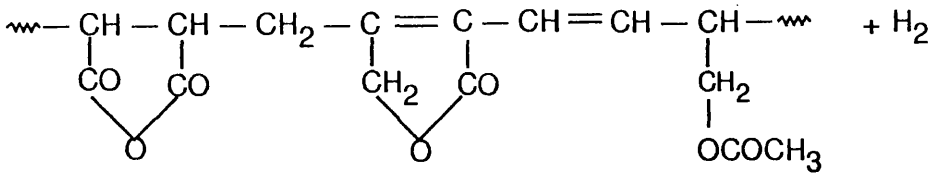
1770 cm^{-1} (VI)



1750 cm^{-1}

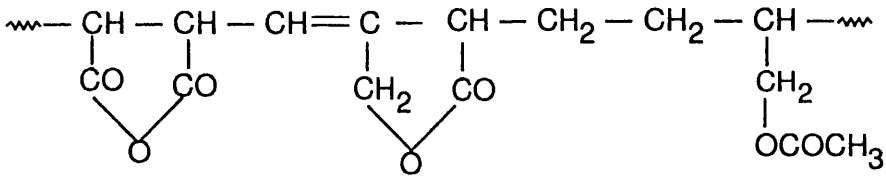
(VII)

or

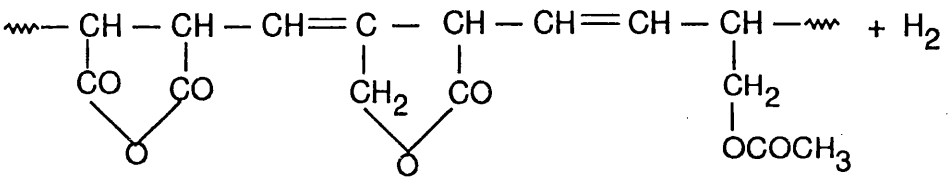


< 1750 cm^{-1} (VIII)

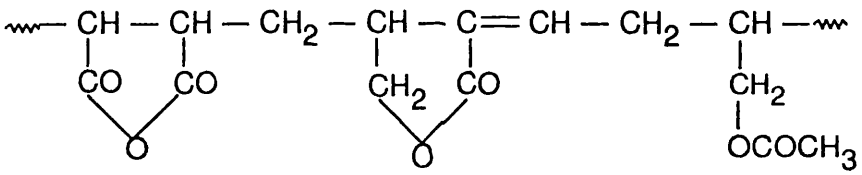
SCHEME 1b Continued



or (IX) 1770 cm^{-1}

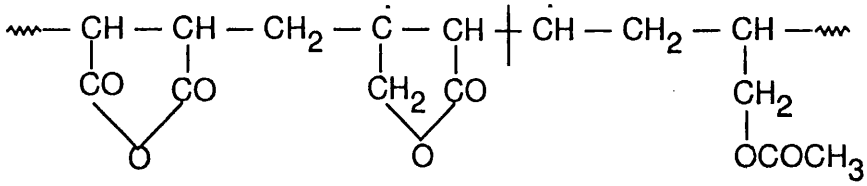


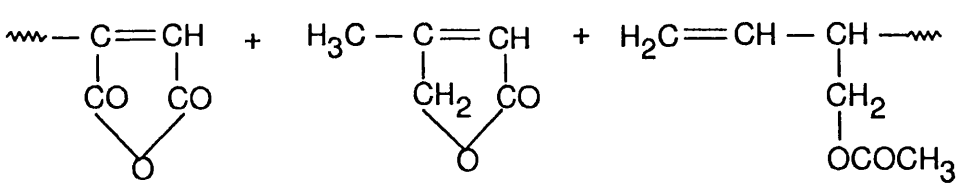
(X) 1770 cm^{-1}



(XI) 1720 cm^{-1}

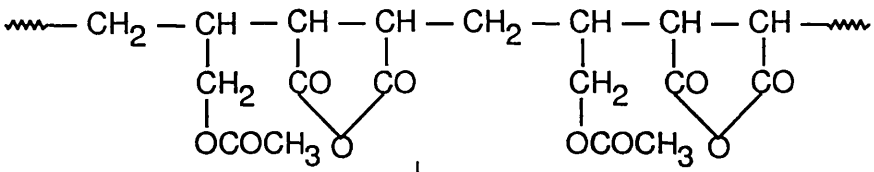
SCHEME 2a

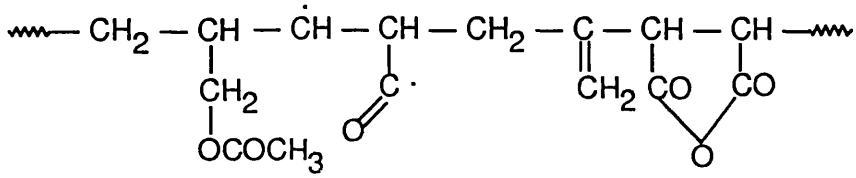




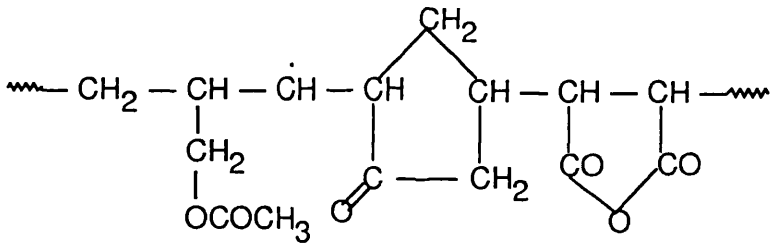
(6)

SCHEME 2b



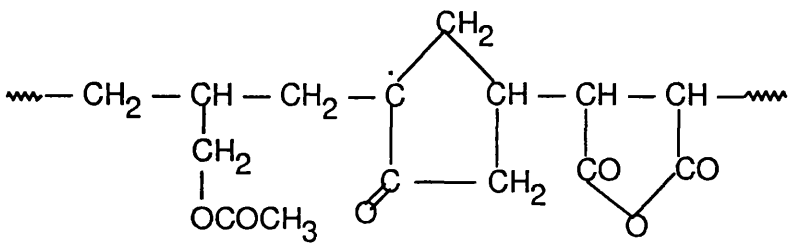


(7)



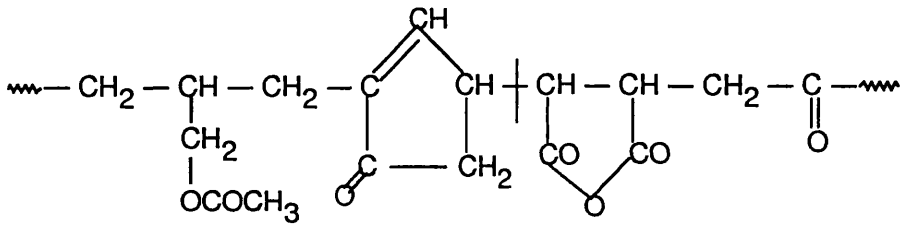
(8)

(XII)

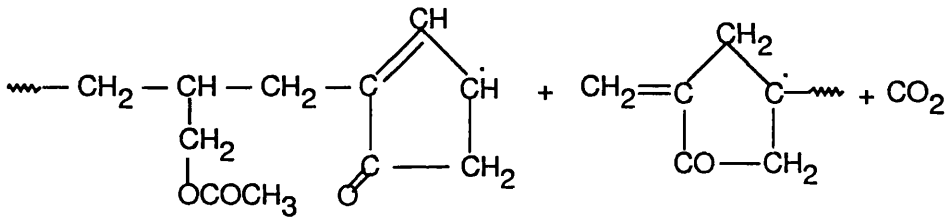


(9)

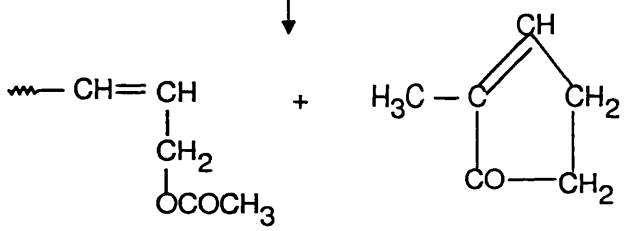
SCHEME 2b Cotinued



(10)



(11)



(12)

(XIII)

CONCLUSION

The copolymer of maleic anhydride with allyl acetate presents two main pyrolysis stages between 200-350°C and 350-500°C. Each of these stages are composed of substages characterised by certain reactions and the evolution of certain classes of products.

During the first degradation stage, there are two substages: the decomposition of some of the anhydride groups with CO_2 and CO elimination and the formation of unsaturation (200-280°C); the elimination of the acetate groups of the allyl acetate units with the formation of pendent vinylidene groups (280-350°C). Also, in this stage, there is the reaction of the decomposing anhydride groups with the formation of γ-lactone rings along the polymeric backbone. This reaction is due to the attack of the carboxyl radical formed through the decomposition of the anhydride on the pendent vinylidene group. Another reaction between these groups leads to cyclic 5-membered ketone rings, but to a lower extent than the lactone rings. The 5 membered ketone rings are formed through the attack of the anhydride on the pendant CH_2 groups.

In the second stage of decomposition, between 350 and 500°C, there is massive breakdown of the structures formed in the first stage with the several fractions of products : tar (cold ring), liquid fraction and a gaseous fraction in which hydrocarbons, H_2, CO, and CO_2 are present.

The second stage is also composed of substages. In first substage, between 350 and 420°C, with a maximum rate of product formation around 380°C, O-containing products such as saturated and unsaturated lactones (dihydrofuranones and furanones) are formed as decomposition products of lactone rings existing in the polymer chain. Another class of O-containing

O-containing compounds formed in this stage are alkyl substituted cyclopentenones and cyclopentanones. Some of aromatic hydrocarbons are also formed in this stage, mainly toluene, xylene and trimeyhylbenzene. In a second substage, between 380-500°C, with a maximum rate at 420°C, only aromatic hydrocarbons such as C4 alkyl and alkenylbenzene are formed.

The MAn—AllAc copolymer decomposes into a large liquid fraction (41.5%), moderate cold ring fraction (24%) and an important amount of residue.

The MAn—AllAc copolymer can be compared with the copolymers of MAn with vinyl acetate and isopropenyl acetate.

The MAn—AllAc copolymer is the first in the studied series of copolymers where decarboxylation occurs prior to deacetylation. The presence of allyl acetate units have a stabilising effect on the copolymer through the formation of pendant vinylidene groups as a result of deacetylation. These groups are active in the formation of species such as cyclic lactone and cyclic ketone rings along the polymer backbone which exert a certain protection at temperatures up to 380°C when breakdown forming O containing products occurs. The pendant vinylidene groups are also active in crosslinking and aromatisation and as a result the polymer forms an appreciable amount of char (16%) at 500°C. From this point of view MAn—AllAc copolymer behaves more like MAn—VA copolymer while the MAn—IPAc copolymer is less stable due to isopropenyl units, in which all the acetate groups are linked to tertiary C atom, which provides the easy route for the thermal dissociation of copolymer.

OVERALL CONCLUSIONS

In this work, a large number of alternating copolymers, along with their respective homopolymers, have been synthesised and their thermal degradation behaviour has been examined. It has proved possible to synthesise by controlled degradation some new materials that cannot be synthesised directly. In addition, the understanding of the thermal degradation mechanisms of these polymers has been advanced, while important information has also been gained about breakdown temperatures and the nature of the degradation products.

For many of the copolymers the degradation was found to consist of two main stages, the first stage forming an intermediate polymeric structure that breaks down at higher temperature. By only degrading the copolymer to the first stage, a new material can be isolated for further synthesis or other uses.

Two features are of importance in relation to the potential usefulness of the intermediate. The first is the separation of the two stages of degradation in temperature, such that backbone scission does not become important before formation of the modified, intermediate structure is complete. Although the maleic anhydride—vinyl acetate copolymer has already found some application in controlled drug release (see Chapter 1) the separation is not ideal. In the present work, it has been shown that the maleic anhydride—isopropenyl acetate copolymer is superior in this respect and is potentially a more useful starting material for drug release applications.

However, in the related copolymer in which the isopropenyl acetate group is replaced by allyl acetate, the side groups are then much more stable and the maleic anhydride unit decomposes first, forming ketonic groups in the backbone and cyclic lactone at higher temperature. It has been found as a

result that in this copolymer the several reactions involved overlap in temperature range and a required intermediate structure cannot be isolated.

The other important feature is structural regularity in the intermediate material formed by controlled degradation.

A good example is the maleic anhydride—isopropenyl acetate (MAn—IPAc) copolymer which forms regularly spaced isolated double bonds in the backbone by elimination of the acetate side groups from each isopropenyl acetate unit. This isolated unsaturation is very regular and can clearly be used for further synthesis.

Another example, the crotonic acid—vinyl acetate (CA—VA) alternating copolymer, also decomposes in two stages. The intermediate is formed mainly from the cyclisation of adjacent acid and ester side units forming lactone rings with the elimination of acetic acid, whilst a secondary reaction is the decarboxylation of acid groups at higher temperature. However, the cyclisation reaction occurs at random and can therefore leave isolated acetate or acid groups, such that the intermediate is not structurally regular.

The vinyl acetate—methacrylic acid (VA—MAA) copolymer also degrades in a similar fashion but it is not completely alternating since it contains a small proportion of 2-4 unit sequences of either monomer. This polymer degrades in three stages. Anhydrisation takes place at lower temperature between adjacent MAA units followed by lactone formation between MAA and VA units. Because of the single monomer sequences and the reactions taking place at random positions, the intermediate does not have any regular structure. It is clear that the main problem with forming intermediate structures is that a single reacting unit can react with either of its neighbours. This leads to some side groups becoming isolated. If it were possible to direct the reaction, in some way, such that a reacting unit could only react with one of its neighbours then a very regular structure will be produced.

The mechanisms of degradation for many of the copolymers used have been elucidated and the behaviour of the alternating copolymers has provided some interesting data on possible synthetic pathways by controlled degradation. Overall, this study has given good insight into the general theory of thermal degradation and much information has been obtained about the thermal behaviour of the polymers and their products of degradation.

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